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Physics. — *A visual spectroscopic method in heterochromatic photometry.* By L. S. ORNSTEIN, Miss J. G. EYMERS and D. VERMEULEN. (Communication from the Physical Institute of the State University of Utrecht.)

(Communicated at the meeting of April 2, 1932.)

1. Some time ago we have built in our Institute a spectral pyrometer in which a monochromator is used in stead of a "monochromatic" filter. If we put our eye at the spot of the last slit of a monochromator we will see the illuminated field in a colour which can be chosen arbitrarily. In this way it is possible for us to compare in that colour the intensity of two lamps of which an image is formed at the same spot.

After the construction of a pyrometer with vanishing wire had been performed in this way, we found in the litterature that HENNING [1]) had used this principle already in 1910, with the only difference that he used a spectroscope in stead of a monochromator.

Now if we see which how much trouble various investigators have worked out methods for the determination of the effective wavelength of filters, it is clear that the method of HENNING had not been used to the extend it deserves. In our opinion the use of a double monochromator [2]) has great advantages as well in respect to the greater spectral purety as in respect to the greater luminosity.

During the last time we have used the monochromator-pyrometer for the solution of several problems, combining the instrument with a lamp relatively or absolutely standardised energitically for the visible. In this way it is possible to perform heterochromatic photometric measurements in a quick and accurate way. We will give a description of the method used for the measurement of:

a. the relative measurement of intensity for a given wavelength;

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[1]) F. HENNING, Z. S. f. Inst. 30, 62, 1910.

[2]) P. H. v. CITTERT, Rev. d'opl. 2, 57, 1923.

b. the measurement of reflection and absorbtion;

c. the measurement of the proportion of distant spectral lines;

d. absolute measurement of intensity;

e. optical pyrometry, determination of the effective wavelength of colour filters;

f. application to the photometry of incandescant lamps.

2. *Description of the apparatus.* In order to compare the brightness of a body with that of a lamp *L* (fig. 1) for a given wavelength we form

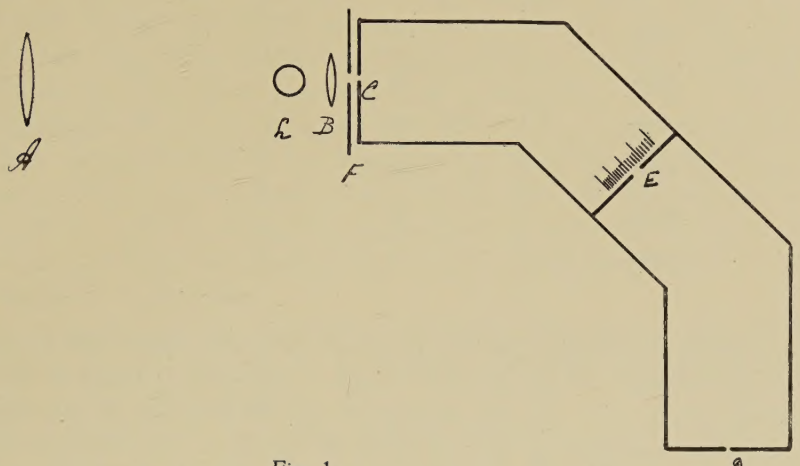

Fig. 1

with the help of a lense *A* an image of the body on the wire of the lamp, which is put before the double monochromator. The eye is put behind the last slit *D* of the monochromator. In order to understand easily the action of the apparatus one should bear in mind that the monochromator forms an image of the eye at the first slit *C* in a given wavelength. This image of the eye can be considered to look at the wire and the image of the body with the help of a lense *B*. *F* is a diaphragm. which is totally filled by the rays originating from the body, the brightness of which we wish to measure. The adjustment of the central slit can been performed with the help of a Helium geisler tube.

From the theory of the double monochromater it appears that the region originating from the monochromator is proportional to the sum of width of the slits *C* and *E* when the last slit is larger than the first and the central slit. This was always the case in our measurements. Table 1 gives the spectral region for a slitwidth of 0.3 mm. The slit width used is indicated at the different applications of the apparatus we describe below.

The method of measuring the spectral region originating from the monochromator may be sketched. An image of the last slit of the monochromater is formed perpendicular to the slit of a spectroscop. The theory of the monochromator shows that we see in this case a parallelogram.

The edges of which can be determined accurately and give the region mentioned.

TABLE I.

Wavelength Å	Spectral region Å	Minimum Region Å
6750	255	43
6135	174	29
5650	132	22
5285	103	17
4995	81	14
4760	65	11
4565	54	9
4403	65	7
4260	37	6

The energy distribution for the case that first and central slit are equal consist of a triangle. If the spectral region is sufficiently small so that the sensitivity of the eye and the energy of the frequencies in the spectral region under consideration may be taken as constant. The effective region coming from the monochromator can be taken half the base of the triangle. In this way table 1 has been constructed. A region of 100 Å can be determined accurate to 1 Å without any trouble in the yellow the accuracy for red and violet is somewhat less.

3. *Relative intensity measurement for a given wavelength.*

Let us take as an example the problem that the intensity of light of given intensity has to be determined for gas discharge tubes as function of the current density. The surface brightness is too large to be compared with those of the pyrometer lamp.

We have therefore put a white screen in apropriate distance of the tube and photometred the screen [1]).

The fact that we have to measure a very homogeneously illuminated surface is a great advantage for the precision of the measurement.

The width of the slits of the monochromator has been chosen in such a way that no disagreable difference in colour occurred between the wire of the pyrometer lamp and the image of the screen. At given current in the lamp to be measured the current of the pyrometer lamp was changed till the brightness of the wire of the pyrometer lamp and the field were equal.

[1]) The way in which the reflective power of the screen depends on wavelength is of no importance for the problem under consideration.

The brightness of the pyrometer lamp was standardised before as a function of the current in the pyrometer lamp circuit in which an accumulator and a precision ammeter were placed. This standardising was operated so that the pyrometer lamp was compared with the screen which was illuminated by a lamp operated on constant current and put in different known distances from the screen. By the change of distance the brightness of the pyrometer lamp for different currents was determined in a proportion of relative brightness going from 1 to 200, where the smallest intensity use is arbitrarily put 1. The standardising for larger brightness was performed in the following way. The constant lamp is put so near to the screen that the pyrometer lamp shows a brightness 200. Now the light is weakened by a neutral filter the brightness found gives immediately the transmission of the filter. Now the lamp is brought so near to the screen that the brightness is much larger than 200 — the square of the distance law now being invalid. If we now put the filter between the lamp and the screen and if the brightness found is less than 200 the intensity of the lamp can be found knowing the transmission of the filter. In this way the apparatus has been standardised for relative intensities between 1 and 10^4 for different wavelengths.

The agreement of the current for which the difference of wire and field disappears for different observers is very good. The accuracy of a single lecture of the current is about 1 %.

The possibility of separating narrow spectral lines is limited by the smaller width of slit for which the image of the wire is not spoiled by diffraction. In column 3 of table 1 the spectral region of minimum dispersion is given. The disturbtion by straylight plays no part when a double monochromator is used.

The accuracy of measurement is the greatest when large homogeneous surfaces are photometred, for small surfaces the precision is much less. In order to attain for capillary tubes the same precision of measurement as for larger surfaces we can proceed in the following way : the pyrometer lamp is replaced by a diffusing white plane with a slit in which an image of the capillary tube is formed ; the surface itself is illuminated from one side by a lamp of which the intensity is known as a function of the current (f.i. measured in the way described above). If we now measure the current intensity at which the image of the capillary disappears in the back ground the brightness can be measured in this way.

It may be urged that it is possible to measure with the spectral pyrometer to a precision of 2 % proportions of intensities up to 10^4. If one should like to do this with the thermoelectric, the photoelectric or the photografic method it would be a very tiresome work.

A further advantage of the visual method occurs for those cases whose electric disturbances make impossible to use the thermoelectric or photoelectric method. As an example we show some measurements of the intensity of a Helium tube in a condensed discharge.

The only other method available is now the photografic method which is used by Mr H. P. BOUWMAN [1]) for this work in our institute. We have measured for several *He* lines the energy emitted pro discharge; for this purpose we have measured the surface-brightness as a function of the discharge-potential. Multiplying this surface-brightness with the number of discharges pro second we get — as Talbot law shows — the intensity pro discharge. In Fig. 2 curve I gives the results of the spectral-pyrometric method curve II those of the photografic method kindly put to our disposal by Mr BOUWMAN; the agreement is very good.

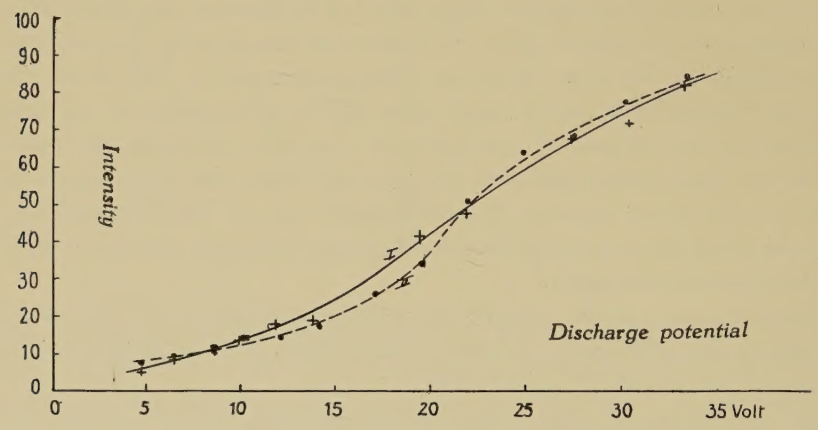

Fig. 2

4. *Measurement of reflexion and absorption.* In order to find the reflective power of a surface the intensity of a band lamp is measured with the pyrometer direct and also reflected in the surface, the current density of the band lamp being constant. The proportion of the brightness found for both cases gives for each wavelength the reflective power.

In order to measure the absorption coefficient a white surface is measured with and without the absorbing substance in the path of light. The precision of these measurements is — as already has been pointed out in the standardising — about 1 %. If there is a strong selectivity the smaller spectral region which can be used plays a part. (Compare table 1.)

The spectral pyrometer is also of great use for the measurement of colours; for this purpose a "normal white" [2]) surface has to be compared with the colours by constant illumination. In fig. 3 the reflective power of an oil-colour (flesh colour) in a painting of JAN SLUYTERS is reproduced as a function of wavelength for perpendicular incidence of the light.

The spectral-pyrometric method furnishes an important way of operating

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[1]) For the electric circuiting comp. Z. S. f. Phys. 43, 839, 1927 and the Utrecht, Dissertation of H. P. BOUWMAN which will appear in a short time.

[2]) We have used „normal weisz" compare Z. S. f. Phys. **10**, 111, 1922.

for the research of the scattering of light in turbid media particularly as large differences of intensity can be measured.

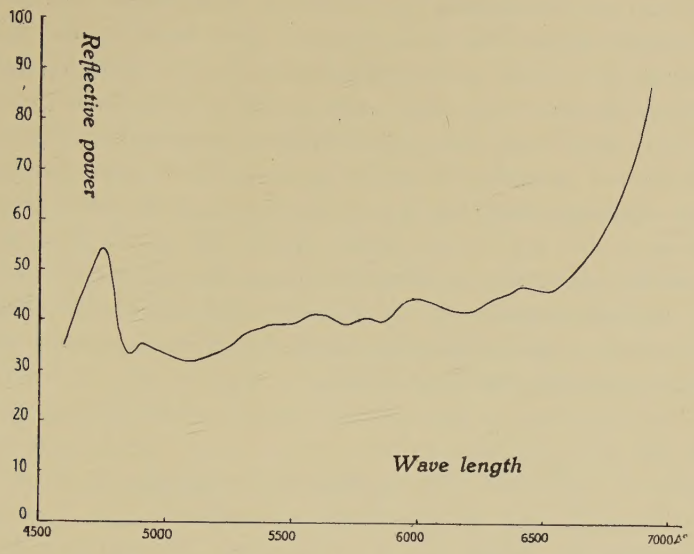

Fig. 3

5. *The measurement of two distant spectral lines with the help of a normal lamp.* In order to compare the intensity in different spectral regions it is necessary to find the correction for the specific properties which shows the apparatus for different wavelengths. With the help of a lamp standardised relatively for energy as a function of wavelength this can be done in the following way.

A white surface is illuminated by a normal lamp of given colour temperature [1]), and the currents of the pyrometer lamp i_{λ_1} and i_{λ_2} are determined for the wavelength λ_1 and λ_2, the spectral region passing the pyrometer may be $\triangle\lambda_1$ and $\triangle\lambda_2$. The proportion of the energies E_1/E_2 can be determined with the help of the Planck formula from the known colour temperature.

The observed energies in $\triangle\lambda_1$ and $\triangle\lambda_2$ are $\triangle\lambda_1\ E_1$ and $\triangle\lambda_2\ E_2$, the pyrometer currents i_{λ_1} and i_{λ_2} are a measure for those energies, which can be used in order to find the skale necessary to which the curves of standardisation of 3 must be shifted.

If one now determines the pyrometric values i'_{λ_1} and i'_{λ_2} for two colours, then in the changed diagram these currents give a direct measurement of the intensities of the spectral lines. The errors of the standardising of the lamp enter to their full value in the result obtained.

6. *Absolute measurements.* If an absolutely standardised lamp is

[1]) For the standardising of the lamp. comp. L. S. ORNSTEIN Journ. optic. Soc. Amer. **20**, 573, 1930.

available it is without further comment clear that intensities may be measured absolutely.

We have used this proceding in order to measure the daylight in different wavelengths. For this purpose we have made pyrometric measurements of a white surface illuminated by the daylight on the roof of the Utrecht Institute. The whole equipment was standardised absolutely with the help of a lamp (absolute energetic standard of the Institute) placed at known distance from the surface. The apparatus seems to furnish an important help for the measurement of the solar energy and the radiation of the sky in the visible, chiefly because it is very easy to interchange the absolutely standardised lamps for different observers. In this way systematic error can be avoided and the results of different observers become much better comparable. Fig. 4 gives some of the results which will be published later more fully.

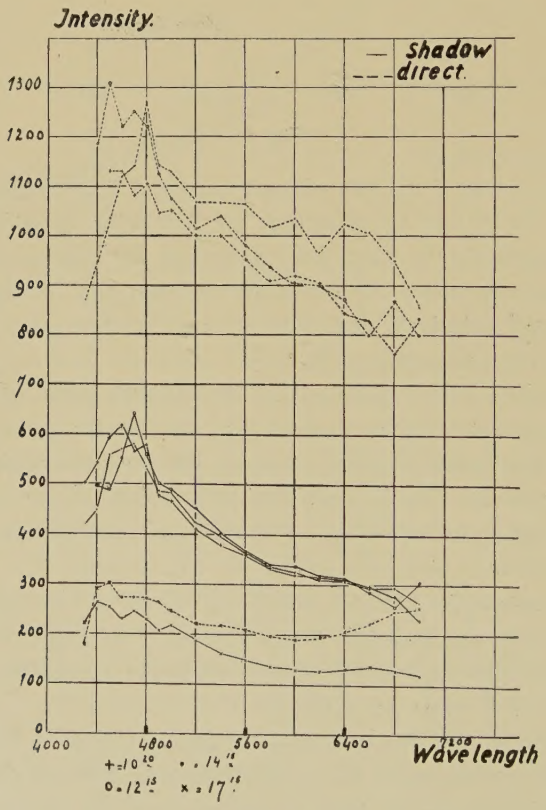

Fig. 4

7. *Optical pyrometry, effective wavelength of colour filters.* As already HENNING has pointed out the spectral pyrometer is very fitted for the pyrometric work in arbitrary wavelength regions with well defined regions of wavelength. The apparatus can also be used in order to determine the

effective wavelength of colour filters used in the optical pyrometer helping in this way to get greater accuracy for this instrument.

The effective wavelength of coloured glass has been calculated by FORSYTHE [1]) and HENNING [2]) on the base of theoretical investigations on the photometric determination of two radiating bodies of different colour temperature. W. DE GROOT [3]) has indicated a somewhat lengthy experimental method for the determination of the effective wavelength.

With the help of the described apparatus the effective wavelength can be determined exactly, and quickly, the use of the monochromator is essential for this work [4]).

If the double monochromator is illuminated with white light and the middle slit is taken out, white light comes from the last slit.

Now we illuminate a white surface with a lamp of given colour temperature f.i. 2500° K. and perform a measurement with the spectropyrometer with the second slit taken out and the filter put in front of the third slit. The pyrometer lamp shows then a temperature of 1400° K. Then the middle slit is put in again and the filter taken away; and the middle slit adjusted till again the surface and the pyrometer wire have the same brightness. The wavelength indicated by the position of the middle slit when this is the case, gives the effective wavelength of the coloured glass. Several observers have determined in our Institute in this way this quantity for a green glass, from their measurements it appears that in the green an accuracy of 2 Å may be attained, which opens the possibility of much precised pyrometric measurements.

8. *Application to the photometry of lamps.* In the measurement of intensity the brightness of two fields is always compared; one field is illuminated by a known the other by an unknown source of light. The LUMMER—BRODHUN prism is generally used in order to compare the fields juxtaposed. Till now only the comparison of light sources of equal spectra distribution was possible with accuracy. When the light sources differ in colour the adjustment gets uncertain and different observers show large differences.

The method used in this paper, to see through a monochromator the world in a colour which can be chosen arbitrarely, can be applied also in the photometer bench in order to observe the field of the LUMMER—BRODHUN in one colour.

We have in a provisory optical bench in which a LUMMER—BRODHUN prism with two fields was mounted-compared two incandescent lamps.

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[1]) FORSYTHE Journ. Opt. Soc. Amer. 4, 305, 1920.

[2]) F. HENNING, Z. f. Phys. **30**, 285, 1924.

[3]) W. DE GROOT, Physica 4, 157, 1924.

[4]) The HENNING apparatus as constructed by SCHMIDT and HAENSCH is less usefull for this work.

It is possible — the white illumination being 40 Lux — to observe differences in brightness for red, green and blue of 1 %.

In our opinion it is possible to characterise lamps comparing them in three colours with the normal lamp; in this way the distribution of energy is sufficiently determined for all technical purposes.

If an absolutely standardised lamp is chosen for the known lamp as a comparison-standard, it is possible to measure absolutely the spectral composition, of a lightsource with the photometer bench.

It is also possible to measure with our method the absolute spectral composition for any lightsource.

It is our opinion that the double monochromator used in the way described can be an important help in heterochromatic photometry.

Physics. — *The spectrum of the solar corona* [1]). By T. L. DE BRUIN. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of April 2, 1932.)

1. *Historical note.*

References to the phenomenon of the solar corona at the time of a total eclips of the sun can be traced through the whole history of mankind [2]). The spectroscopic study of the solar corona started in the same year 1868 that the helium in the sun was discovered. The next year 1869 brought the discovery of the mysterious "coronium".

At the total eclips of August 18, 1868 POGSON, RZIHA and TENNANT observed the continuous spectrum of the corona, but no absorption or emission lines. At the total eclips of August 7, 1869, HARKNESS and YOUNG independently observed the green coronal line and YOUNG proved that it has a truly coronal origin. YOUNG's measures of the line placed it at 1474 K (KIRCHOFF scale) or in the modern scale at λ 5317. Many additional observations later continued to place it at or near 5317 *A*. At the eclips of 1893 FOWLER photographed nine coronal rings with a slitless spectrograph, all of which agree in position with selected lines reported as of coronal origin in the 1886 eclips. At the eclips of 1898 FOWLER, SHACKLETON and W. J. LOCKYER made the interesting discovery that the famous green coronal bright line is not at 5317 but at 5303.

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[1]) Preliminary note: Nature. March 26, 1932.

[2]) A very extensive report over: "Eclipses of the Sun" by S. A. MITCHELL. Chap. 3. Handbuch der Astrophysik. Bd. IV, p. 231.

Data before 1918 see: LICK. Obs. Bull. X. Nr. 318 343, p. 8. 1918 1923 by W. W. CAMPBELL a. J. H. MOORE. A short and popular note over: Kosmische spectra, see: T. L. DE BRUIN, Hemel en Dampkring. April. Mei. 1931.

Since 1893 also more coronal lines farther to the violet have been detected at several expeditions in the years 1896, 1898, 1900, 1901, 1905, 1908. On August 21, 1914 CARRASCO and independently BOSLER and BLOCK discovered a new bright line in the red at λ 6374. More accurate determinations of wavelengths have been made at the eclipses in 1918, 1922, 1926, 1929 and 1930.

Since 1869 the time spent in photographing the coronal spectrum has amounted to a grand total of about one hour, an average of one minute per year. At the eclips of May 9, 1929 GROTRIAN [1]) detected a new line at 6704 and at the October eclips 1930 MITCHELL [2]) discovered a new line still farther to the red at 6776. Up to the present the total lines ascribed to coronal origin may be fifteen although a few lines may still be suspicious. The most characteristic wavelengths are at:

8.	6776	6.	4086
4.	6704	8.	3987
15.	6374	15.	3601
20.	5303	6.	3454
6.	4231	20.	3388

2. *Attempts to explain the corona and its spectrum.*

The spectrum of the corona has three separate characteristics: first the bright line spectrum of "coronium" existing only in the inner corona and extending on the average to about 200.000 km. from the sun's edge; second, the continuous spectrum of the middle corona and third the FRAUNHOFER lines showing feebly in the outer corona. The corona has been observed to the enormous distance of ten million miles of the sun. Numerous authors have tried to explain these characteristics.

From the very extensive literature concerning this subject we mention the papers and ideas of NEWCOMB (1887) [3]), Sir NORMAN LOCKYER [4]) 1887 (chemical dissociation theory), HUGGINS [5]) 1885 (electrical theory), BIGELOW [6]) 1889 (magnetic theory), EBERT [7]) 1893 (electro-magnetic theory), SCHAEBERLE [8]) (mechanical theory), SVANTE ARRHENIUS [9]) 1908 (radiation pressure theory), SCHWARZSCHILD [10]) 1906 (electron gas theory).

From the attempts to explain especially the bright line spectrum of

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1) GROTRIAN, Zs. f. Astr. **2**. 106. 1931. **3**. 199. 1931.
2) MITCHELL, Astr. Journ. **75**. 1. 1932.
3) NEWCOMB, Pop. Astr. 6th. ed. 1887.
4) LOCKYER, Chemistry of the Sun. 1887.
5) HUGGINS, Proc. R. S. London. **39**. 108. 1885.
6) BIGELOW, Solar Corona discussed by spherical harmonix. 1889.
7) EBERT, Astronomy a. Astrophysics. **12**. 804. 1893.
8) SCHAEBERLE, Contr. Lick. Obs. N⁰. 4.
9) ARRHENIUS, Worlds in the Making. 1908.
10) SCHWARZSCHILD, Astr. Mit. Sternwarte. Göttingen. **13**. 63. 1906.

"coronium" we mention the papers of NICHOLSON [1]) (1911). NICHOLSON tried to explain the coronium lines as emission lines of the hypothetical elements "proto-fluorine" and "coronium", atomconfigurations with nuclei having a charge of 5^e and 7^e. PANNEKOEK [2]) (1922) has assumed that the coronal lines may be due to *Ca* III. More recently FREEMAN [3]) (1928) tried to explain the spectrum as emission of neutral argon. MECKE and WILDT [4]) (1930) incline to believe that the lines may be "Raman-lines". ROSENTHAL [5]) (1930) tried to explain the line spectrum as emission of the helium atom in special stages. Scientific criticism however has shown that none of these theories can be hold upright and now 63 years after its discovery "coronium" is still a mystery. Ideas however have been changed the last five years, after BOWEN's famous explanation (1928) of the mysterious "nebulium" [6]). Forbidden lines in the ionised atoms of oxygen and nitrogen have been recognised in the strong nebular lines. This idea also brought forward the explanation of the famous green Auroral line 5577 (MC. LENNAN, 1928) [7]) as due to a forbidden combination in neutral oxygen. An investigation by BOWEN and MENZEL [8]) to explain the coronium lines in the same way did not have success. EDDINGTON [9]) has shown that on account of the great energy of the sun "coronium" cannot find its explanation from atoms in the corona in metastable states. However the present writer assumed that the source of the coronium lines would be found among the elements in the top part of the periodic table by methods similar to those undertaken by BOWEN. After trying to solve the problem with the ionised elements, with negative results, a systematical investigation was made with the neutral elements. The following paragraphs will show that the atom of neutral oxygen is responsible for the main lines of the mysterious "coronium".

3. *The spectrum of neutral oxygen.*

The spectrum of neutral oxygen has been investigated and analysed by several authors namely RUNGE and PASCHEN [10]), HOPFIELD [11]), MC. LENNAN [12]), PASCHEN [13]) but especially by FRERICHS [14]). FRERICHS

[1]) NICHOLSON, M. N. 1911 1916.
[2]) PANNEKOEK, B. A. N. **1**. 127. 1922.
[3]) FREEMAN. Astr. Journ. **68**. 177. 1928.
[4]) MECKE a. WILDT, Zs. f. Phys. **59**. 501. 1930.
[5]) ROSENTHAL, Zs. f. Astr. **1**. 115. 1930.
[6]) BOWEN, Astr. Journ. **67**. 1. 1928.
[7]) MC. LENNAN, Proc. R. S. London. **120**. 327. 1928.
[8]) BOWEN a. MENZEL, Pub. Astr. Soc. Pac. **40**. 335. 1928.
[9]) EDDINGTON, M. N. R. A. S. **88**. 134. 1927.
[10]) RUNGE a. PASCHEN, Ann. d. Phys. **61**. 641. 1897. Astr. J. **8**. 70. 1898.
[11]) HOPFIELD, Astr. J. **59**. 114. 1924. Phys. Rev. **29**. 923. 1927. **37**. 160. 1931.
[12]) MC. LENNAN, Proc. R. S. London. **1**. 1927. Phil. Mag. **6**. 558. 1928.
[13]) PASCHEN, Die Naturw. **18**. 752. 1930. Zs. f. Phys. **65**. 1. 1930.
[14]) FRERICHS, Phys. Rev. **34**. 1239. 1929. **36**. 398. 1930. **36**. 1460. 1930.

measured the spectrum with high dispersion (6.5 m. grating) between λ 8800 and λ 3800 and in the ultra violet between λ 1200—700 (1 m. grating). The deepest terms in the spectrum are:

$2p\,^3P_{210}$: 109837, 109679 109610 and the metastabile terms $^1D_2 =$ $= 93970$ and $^1S_0 = 76045$. These terms are of special interest because the $^1D_2$—$^1S_0$ combination, the line 5577, has been found to be by Mc. LENNAN the typical green Auroral line. The combinations $^1D_2$—$^3P_2$ 6300 and $^1D_2$—$^3P_1$ 6364 detected by PASCHEN and HOPFIELD in the laboratory are, as the green line 5577, typical lines for the spectra of the Nebulae [1]) and Novae [2]).

Practically all the O 1 lines have been classified by FRERICHS. Still there are a few isolated groups of lines not classified or connected with known O I terms. These groups are:

I.	(4)	6654.121	15024.14	II. (1)	6266.692	15952.98
	(5)	6374.292	15683.64	(2)	6264.346	15958.95
	(4)	6366.282	15703.42	(5)	6261.314	15966.68
				(1)	6258.965	15972.67
				(3)	6256.616	15978.67

III.	(3)	5995.198	16675.43
	(1)	5993.102	16681.24
	(2)	5991.852	16684.72
	(1)	5991.255	16686.39

and in the far ultra violet:

IV. A group of 5 lines around 756 A.
V. The triplet: (0) 770.70 (1) 770.28 (2) 769.39.
VI. A doublet at 756 A.
IV. A group of 5 lines around 792 A.

The groups III and V can be interpreted as combinations of a new high term $5s\,^3D_{321}$ —20135.3; —20141.1; —20142.8 with the known terms $3p\,^3P_{2\,10}$ —3459.8; —3456.4 and the ground triplet. The assignment of inner quantumnumbers in the $^3P_{2\,10}$ needs further investigation. The groups IV, VI and VII are combinations with new high terms —16506; —22473; —23780 and the ground triplet. At present it seems however not possible to check these new high terms. Only the groups I and II need further interpretation and just these groups are connected with radiation in the solar corona.

4. *Coronal lines connected with new deep terms in O I.*

Far the most interesting groups of lines in the neutral oxygen are the groups of lines I and II. These lines can be written in the following multiplet. It should be noticed that the termvalues of the new deep terms

[1]) PASCHEN, Zs. f. Phys. **65**. 1. 1930. BOWEN, Phys. Rev. **36**. 600. 1930. GROTRIAN, Zs. f. Phys. **60**. 302. 1930.

[2]) GROTRIAN, Zs. f. Astr. **2**. 78. 1931.

P, Q, R, X, Y, Z are fixed by assuming that the remaining line of the group 6654.121; 15024.14 is a combination with the known deep metastabile level $^1D_2$.

Without speculation it seems at present not possible to determine the nature of the new terms *P, Q, R, X, Y, Z*. We do hope that the Zeeman-effect of the line 6374 will give us the answer. Plans are projected in this laboratory for an investigation in this direction.

Combinations between the levels *XYZ* and the ground triplet ^3P would give lines under λ 3300. In this region the observation data of the coronal spectrum is very poor. Only exist measurements by DESLANDRES 1893

NEW MULTIPLET IN O I.

		R	Q	P	$^1D_2$
		94898	94905	94925	93970
X	79221	—	5. 6374.292 15683.64	4. 6366.282 15703.42	—
Y	78946	1. 6266.692 15952.98	2. 6264.346 15958.965	3. 6256.616 15978.67	4. 6654.121 15024.14
Z	78932	5. 6261.314 15966.68	1. 6258.95 15972.67	—	—

(Annales du Bureau des Longitudes t. V) λλ 3164; 3170; 3237 and by LEWIS (1908) λ 3288. It should be noticed that the combination $^3P_2$—*Y* gives 3236.3 and $^3P_3$—*X* 3289.7.

Now it is possible from the new terms *P, Q, R* and the known deep terms: $^3P_2 = 109837$ $^1D_2 = 93970$ $^1S_0 = 76045$
$^3P_1 = 109679$
$^3P_0 = 109610$
to deduce the characteristic lines of the solor corona in the red and the famous green "coronium" line 5303.

Int.	Corona		Laboratory		Termcombination
	λ obs.	ν obs.	ν calc.	λ calc.	
8	6776	14754	14754	6776	2p $^3P_1$ — P
4	6704	14912	14912	6704	2p $^3P_2$ — P
15	6374	15684	15684	6374	Q — X
20	5303	18852	18853	5302.7	R — S

5. *Calculation of coronal lines from laboratory data.*

At present no high precision can be claimed for the coronal wavelengths. Several reasons have influence on the data as: diffuse nature of the lines, instruments with small dispersion, spectrograms on films, slitless photographs, incertainty in applying the DOPPLER correction, because at the present time we know nothing regarding the rotation of the corona.

But also some of the wavelengths of neutral oxygen necessary for the calculation of coronal lines need higher precision especially the red Nebulae lines 6300 and 6364. However we will see which values of the coronal lines can be deduced from all the laboratory data at present available.

Coronal line 6776.

This line can be determined from the following lines of neutral oxygen.

1	6363.88	15709.35	HOPFIELD
3	6364.07	15708.88	PASCHEN
4	6654.121	15024.14	FRERICHS
3	6256.616	15978.67	FRERICHS
4u	6256.60	15978.71	PASCHEN.

From these data and the termscheme (see figure) a simple calculation gives as minimum and maximum values 6775.58 and 6775.82, with a mean of *6775.70.* There are only *two* determinations of this new detected red line. MITCHELL finds a mean of 6775.90 No DOPPLER-correction has been applied. The calculated value 5775.70 agrees certainly with the observation because MITCHELL remarks: "The last digit means nothing, and that in tenths of angstroms means little. We shall therefore assume the wavelength to be 6776."

Coronal line 6704.

For the calculation of this coronal line we have the following neutral oxygen lines.

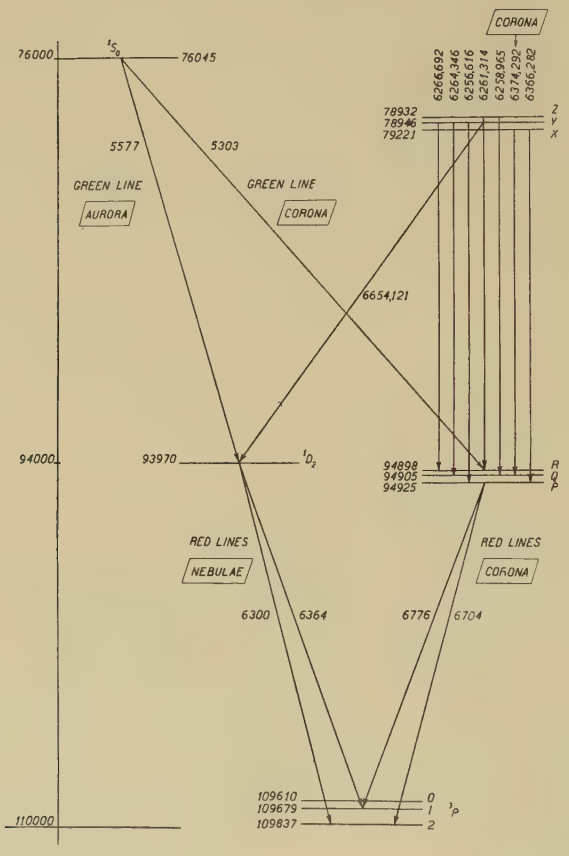
4	6300.23	15868.05	HOPFIELD
5	6300.03	15868.56	PASCHEN
4	6654.121	15024.14	FRERICHS
3	6256.616	15978.67	FRERICHS
4u	6256.60	15978.71	PASCHEN

Calculation from these wavelengths gives as minimum and maximum values 6703.25 and 6703.50 with the mean of *6703.37.* For this coronal line two determinations are available. GROTRIAN who discovered this line gives 6704 ± 2. After the detection of this line DAVIDSON and STRATTON measured the line on old plates of the 14 Jan. 1926 eclips (Observatory 53.211.1930) and give the value 6703.36. Both determinations agree with the calculated value.

Coronal line 6374.

This is the only line observed in the laboratory. FRERICHS gives the value

6374.292, PASCHEN's value is 6374.83. The last value however can not have high precision. MITCHELL measured this line in the coronal spectrum and



DEEP ENERGY LEVELS IN NEUTRAL OXYGEN, OI.

finds as a weighted mean from 6 determinations on 6 films running between 6374.09 and 6374.51 a mean of 6374.28. Also this value agrees with the data from the laboratory.

Coronal line 5303.

In the calculation of this coronal line is involved the famous green Aurora line 5577. High precision measurements are for this line available.

5577.350	17924.70	BABCOCK [1])
5577.341	17924.73	MC. LENNAN [2])
5577.348	17924.70	CARIO [3])

[1]) BABCOCK, Astr. J. **57**. 209. 1923.
[2]) Mc. LENNAN Mc. LEOD, Proc. R. S. London, 115. 515. 1927.
[3]) CARIO, Zs. f. Phys. **42**. 15. 1927.

Coronal line	Author	Eclips	Apparatus	Comparison	Wavelength	References	Remarks	Wavelength from laboratory data
6776	MITCHELL	Oct. 1930 Niuafoou	4 inch grating; 6 „ grating 1e order. Dispersion: ± 10.9 A/m.m. slitless.	Chromospheric lines	6775.90	Astr. J. **75**. 1. 1932	2 determinations on 2 films: 6775.80 and 6776.00	6775,58 – 6775,82
6704	GROTRIAN	May 9, 1930 Takengon	*a*). 3 prisms. Dispersion: 6700—4400 150—16.4 A/m.m. *b*). 3 prisms. Dispersion: (6000)—3900 120—12 A/m.m.	Prominence lines and atmospheric lines	6704 ± 2	Zs. f. Astr. 2. 106. 1931	6704 by extrapolation of HARTMANN formel	6703.25—6703.50
	DAVIDSON and STRATTON	Jan. 14, 1926 Benkoelen			6703.36	Obs. 53. 211. 1930.	The line has been measured after the discovering by GROTRIAN	
6374	CARRASCO	Aug. 21. 1914 Theodosia	Plane grating 7 c.M. 15000 lines per 5 c.M.	Only the reference lines H_α D_3 and H_β	6373.87 ± 0.036	C. R. Paris. **159**. 741. 1914		6374.292 (FRERICHS) 6374.24 (HOPFIELD) 6374,83 (PASCHEN)
	BOSLER and BLOCK	Aug. 21. 1914 Strömsund	3 prisms. Dispersion: 6560—5180. Length = 6.4 c.M.	Diffuse light of the sky	6374.5 ± 0.2	C. R. Paris. **159**. 768. 1914		
	MITCHELL	See above	See above	See above	6374.28	Astr. J. 75. 1. 1932	6 determinations on 6 films. Values run between: 6374.09—6374.51	
	DAVIDSON and STRATTON	Jan. 14. 1926 Benkoelen	2 prisms; 60°; $4^1/_2$ inches base; slit.	Prominence lines	6374.8 ± 0.2	Mem. R.A.S. Vol. LXIV. part. IV. p. 105. 1927		
	LYOT	Without eclips 1931	1 prism; dispersion 11 A/mm.	?	6374.75 ± 0.15	C. R. 5. 443. 1932	width of the line ± 1.3 A.	
5303	CAMPBELL and MOORE	June 8. 1918 Goldendale	3 prisms; slit. Dispersion: 28.4 A/mm.	Iron arc	5302.78	Lick Obs. Bull. x. 318. p. 13. 1918.	Correction for solar rotation —0.035	5302.56—5302.70
	DAVIDSON and STRATTON	Jan. 14. 1926 Benkoelen	See above	Prominence lines	5302.8 ± 0.2	Mem. R.A.S. Vol. LXIV. part. IV. p. 105. 1927		
	MITCHELL	Oct. 1930 Niuafoou	See above	See above	5302.91	Astr. J. 75. I. 1932	8 determinations on 8 films. Values run between: 5302.63—5303.04	
	LYOT	Without eclips 1931	Conc. grating 14.5 c.M. Dispersion; 1.2 A/mm.	?	5302.85 ± 0.03	C. R. 5. 443. 1932	Width of the line 1.3 A.	

For the calculation of the green coronal line we need further the following oxygen lines:

4	6654.121	15024.14	FRERICHS
1	6266.692	15952.98	FRERICHS
5	6266.85	15952.58	PASCHEN

Minimum and maximum values derived from these data give 5302.56 and 5302.70 with a mean of 5302.63.

For this line more measurements in the corona spectrum are present but even for this line no very high precision can be claimed. Some authors apply an estimated value for DOPPLER shift other do not.

ADAMS, ST. JOHN and WARE [1]) give 5303.06. CAMPBELL and MOORE [2]) give 5302.78. DAVIDSON and STRATTON [3]) give 5302.80 ± 0.2. SLIPHER [4]) gives 5302.8. The new determinations of the 1930 eclips run between 5302.63 and 5302.98.

It is a pitty that several authors do not give their probable error. The older determinations before 1918 give mostly 5303 as a round value. However sometimes a much lower value 5302.4 (NAEGAMWALA 1898) has been found. It seems to have no meaning to take a mean of all the known values because the dispersion and resolving power of the several instruments are quite different and also the circumstances. One gets the impression that the determination of this green line has a tendency to lower value as already CAMPBELL and MOORE notice: "Our wavelength of the green line (5302.78) places it farther to the violet than we had expected." The agreement between the value calculated from oxygen lines and the observed values can be said to be sufficient. It is hoped that in the future new and still better data can be obtained from the coronal spectrum.

Further it should be noticed that in all the calculations the oxygen line 6654.121 comes in, only determined by FRERICHS. An error in this wavelength determination is involved in all the calculated coronal lines. At present nobody has succeeded to produce the green coronal line in the laboratory. If so it could give us another check [5]).

Recently LYOT { C. R. PARIS **191**, 1930. p. 834 / C. R. PARIS N°. 5. Feb. 1932 } succeeded to photograph the green coronal line 5303 and the red line 6374 without an eclips. He used very large dispersion. LYOT found that the width of the coronal lines is of the order of 1.3 A. His determinations and those of other authors are given in the following table.

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[1]) ADAMS, ST. JOHN, Miss WARE, Publ. Astr. Soc. Pac. **30**. 251. 1918.

[2]) CAMPBELL a. MOORE, Lick. Obs. Bull. N°. 318, p. 13. 1918.

[3]) DAVIDSON a. STRATTON, Mem. R. A. S. p. 143. 1927.

[4]) SLIPHER,

[5]) It should be noticed that the older measurements are given in Rowland scale. For reducing to international scale one have to abstract 0,18 A:

6. *Unidentified coronal lines in the violet.*

Although the three red lines and the green coronal line now are identified as having their origin in neutral oxygen, in the violet part of the coronal spectrum are still several unidentified lines. It seems quite possible that some of these lines are due to neutral nitrogen. Some indications point in that direction. If so it turns out that the mysterious "coronium" recognized over half a century is identical with the most important gases of our own atmosphere although the conditions in the suns atmosphere are certainly quite different.

Finally the writer is particularly indebted to Professor P. ZEEMAN who took the greatest interest in the progress of the work.

University of Amsterdam, Laboratory "Physica".

March 22, 1932.

Physics. — *On a method of correcting for incomplete thermal isolation in measurements of small heat capacities.* By W. H. KEESOM and J. A. KOK. (Communication N°. 219c from the Kamerlingh Onnes Laboratory at Leiden.)

(Communicated at the meeting of April 2, 1932.)

§ 1. *Introduction.* In measuring heat capacities at the lowest liquid helium temperatures after NERNST and EUCKEN's method it is sometimes difficult to obtain a thermal isolation of the calorimeter block that is sufficiently high so as to determine the correction for the heat exchange with the surroundings after the simple methods used till now.

As a matter of fact, we only lately succeeded in obtaining regularly at temperatures below 2° K such a high vacuum in exhausting the helium gas admitted in the process of cooling the block.

In previous experiments in this laboratory this was not always possible.

The consequence of this, owing to the extremely small heat capacities [1]) that occur at these temperatures, was that the time-rate of the temperature after the heating was rather large and that the temperature increase caused by the heating vanished in a few minutes, if not seconds.

To be able to perform measurements also in this case, we worked out an accurate method for correcting for the heat exchange during the measurement.

§ 2. *The heat exchange law at extremely low temperatures and high vacua.*

a. Application of the method just-mentioned being only allowed if the

[1]) So the measuring core used in experiments on the specific heats of tin and zinc (Comm, Leiden, No. 219a, These Proceedings **35**, 143, 1932) had a heat capacity at 1.76° K of 0.00084 cal/°K.

temperature variation caused by heat exchange is proportional to the temperature difference we thought it not superfluous to test this proportionality for the circumstances of the measurements under discussion. As a matter of fact there are different reasons that might invalidate it, such as:

1. the relations derived for heat conduction in the extremely rarefied gas state[1]) (mean free path large compared with the linear dimensions of the space between the bodies exchanging heat) might not be valid at these extremely low temperatures,

2. the variations of the heat capacity of the block in the temperature interval of the experiment might intervene prohibitively,

3. the ratio heat exchange: temperature difference might change appreciably in the temperature interval mentioned[2]),

4. the vacuum might be not sufficiently high to allow us to apply the laws of the extremely rarefied gas state.

It is probably the point mentioned under 2. that at the lowest temperature will first restrict the applicability of the method presented. The data presented further in this § prove, however, that at the temperature of 1.3° K a temperature interval of about 0.1 degree is still permitted[3]).

b. Fig. 1 and 2 show typical examples of the galvanometer readings during a measurement of heat capacities. They belong to a series of measurements on zinc and tin[4]), made May 21th 1931 and March 25th 1931. The temperatures at the beginning and at the end of the heating were resp. 1.272 to 1.362° K[5]), and 2.262 to 2.322° K[6]). The observed points are indicated by ⊙.

c. We make the following suppositions:

1. The heat capacity of block and core is constant ($=c$) during the period considered,

2. The temperature ($=T$) of block and core is uniform[7]),

3. Heat exchange is proportional to temperature difference ($k=$ heat exchange between block with core and surroundings per degree temperature difference and per second),

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[1]) Cf. J. H. A. TER HEERDT. Thesis for the Doctorate, Utrecht, 1923, p. 6.

[2]) In consequence of variation of the accomodation coefficient with temperature, or already in accordance with the molecular theory of heat exchange between corrugated surfaces. Cf. M. KNUDSEN, Ann. d. Phys. (4) **34**, 593, 1911. J. H. A. TER HEERDT, l. c., pag. 135.

[3]) The application of this method made in experiments Ia and *b* of Jan. 28th, 1931. cf. Table I Comm. N°. 219*b* is, however, somewhat doubtful.

[4]) W. H. KEESOM and J. N. VAN DEN ENDE, These Proceedings, **35**, 143, 1932. Leiden Comm. N°. 219*b*.

[5]) N°. Ia of Table II, Comm. N°. 219*b*.

[6]) N°. I*b* of Table I, Comm. N°. 219*b*.

[7]) The measuring current used for the resistance thermometer is supposed to be small. The small constant temperature difference between thermometer and core does not interfere with the following deductions.

4. The heat production in the heating period is constant ($=l$ cal. per sec.),

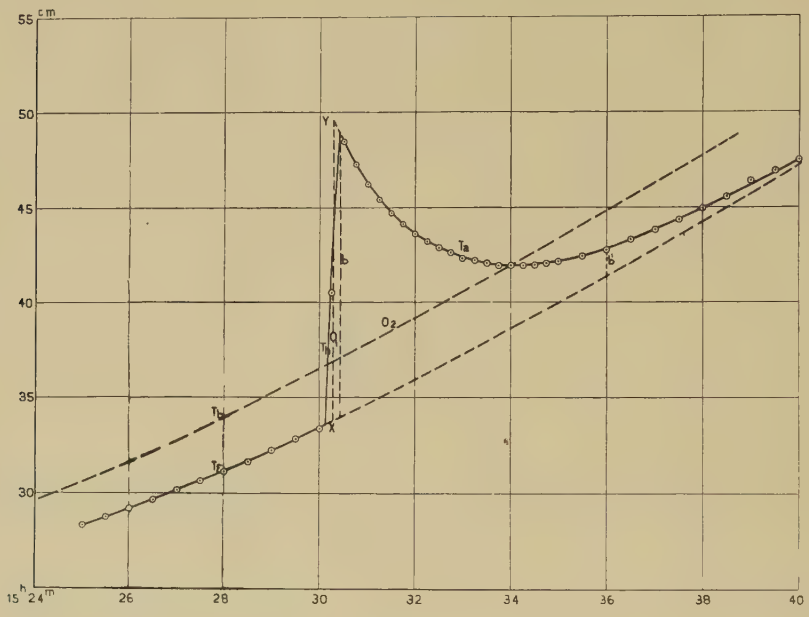

Fig. 1

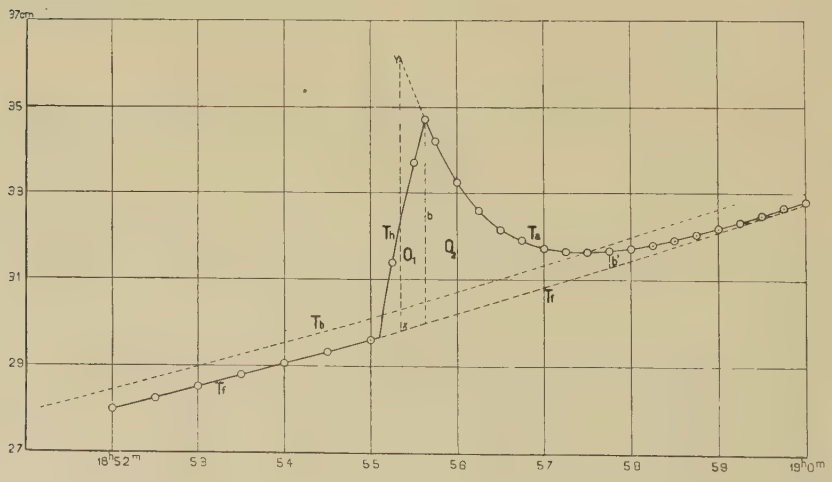

Fig. 2

5. The temperature of the surrounding bath (T_b) is some regular function of time.

We count the time t from the moment of beginning of the heating. The temperature of the bath may be

$$T_b = f(t).$$

If we suppose for a moment that no heating occurred, the temperature of the block would be e.g.

$$T_f = g(t).$$

This coïncides with the real temperature of the block in the fore-period $t<0$. The real temperature in the heating-period we call T_h, that in the after-period T_a.

It easily follows:

1. *heating-period:*

$$T_h - T_f = \frac{l}{k}\left(1 - e^{-\frac{k}{c}t}\right), \quad \ldots\ldots\ldots \quad (1)$$

2. *after-period:*

$$T_a - T_f = be^{-\frac{k}{c}(t-t_1)}, \quad \ldots\ldots\ldots \quad (2)$$

if heating is stopped at $t=t_1$, and

$$b = \frac{l}{k}\left(1 - e^{-\frac{k}{c}t_1}\right). \quad \ldots\ldots\ldots \quad (3)$$

From (1) and (2) with (3) we derive:

$$kO_1 = k\int_0^{t_1}(T_h - T_f)\,dt = lt_1 = bc, \quad \ldots\ldots\ldots \quad (4)$$

$$kO_2 = k\int_{t_1}^{\infty}(T_a - T_f)\,dt = bc \quad \ldots\ldots\ldots \quad (5)$$

Hence:

$$kO = k(O_1 + O_2) = lt_1.^{1}) \quad \ldots\ldots\ldots \quad (6)$$

c. For testing the proportionality of temperature variation and temperature difference we may measure the surfaces O and O_2 with a planimeter[2]), in diagrams such as Fig. 1 and 2 after having drawn a plausible curve for T_f. We then derive $\frac{l}{k}$ and $\frac{c}{k}$, and compare the values of $T_h - T_f$ and $T_a - T_f$ calculated from (1) and (3) with the observed ones of Fig. (1) and Fig. (2).

---

[1]) The equations (5) and (6) can be directly derived by comparing what really happens with what would happen if no heating occurred.

[2]) Instead of finding the whole surface O_2 by planimeter, for which extrapolation to $t=\infty$ would be necessary one can take the surface O_2' to any vertical boundary (e.g. b') and add $b'\,c/k$, c/k being a provisional constant.

For the experiment represented in Fig. 1 the numbers are:

$O = 37.7$, $O_2 = 35.4$, $O_1 = 2.3$, $O_2' = 32.3$ cm min,

$b = 14.80$, $b' = 1.45$ cm of galvanometer scale,

$t_1 = 0.30$ min.

Hence $c/k = 2.42$ min [1]), $l/k = 125.5$ cm. galv. sc.

The correspondence between the formulae and the observed results may be judged from Fig. 3 and 4, where the abscissa is given in cm of galvanometer scale and the difference (cm obs.-calc.) between the observed and calculated values is taken as ordinate [2]).

For the experiment represented in Fig. 2 the numbers are:

$O = 5.33$, $O_2 = 3.94$, $O_1 = 1.39$, $O_2' = 3.61$ cm min,

$b = 4.72$, $b' = 0.39$ cm of galvanometer scale,

$t_1 = 0.533$ min.

Hence $c/k = 0.835$ min $= 50.1$ sec [3]), $l/k = 9.994$ cm. galv. sc.

From this and a number of similar tests we conclude that under the conditions of these experiments the temperature variation caused by heat exchange is proportional to the temperature difference.

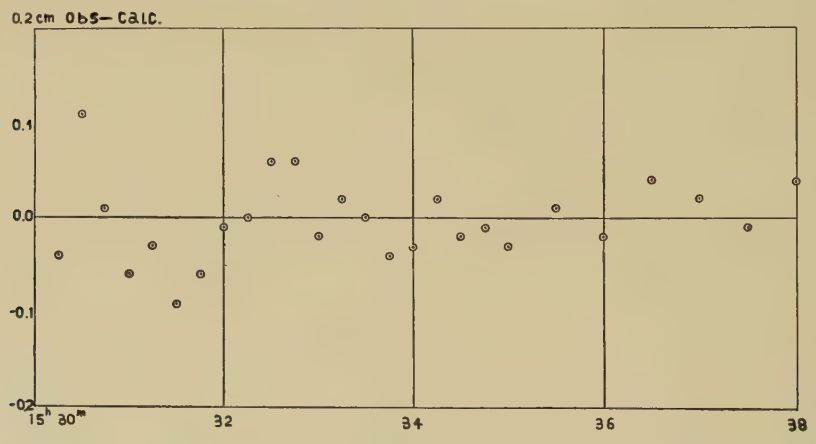

Fig. 3

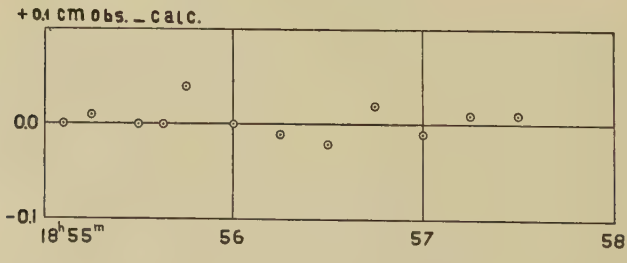

Fig. 4

[1]) The pressure in the vacuum space was not measured. An estimation from the heat transport gives 1.5×10^{-6} mm. mercury.

[2]) In comparing these deviations we recognize the larger activity of the traffic at day hours compared with evening hours.

[3]) In this case the pressure is estimated to have been 2×10^{-5} mm. mercury.

§ 3. *Correction for the heat exchange.*

a. From (5) and (6) follows for the "ideal temperature increase", i.e. the temperature increase that would have been observed if there had been no heat exchange with the surroundings:

$$\frac{lt_1}{c} = O/O_2 \,.\, b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From this and the heat lt_1 supplied, the heat capacity c follows immediately [1]).

a'. A better method is derived as follows. By integration of (2) we find

$$kO_2' = c\,(b-b'),$$

which gives with (5):

$$\frac{b-b'}{O_2'} = \frac{b}{O_2}.$$

From (7) then follows

$$\frac{lt_1}{c} = b + \frac{O_1}{O_2'}(b-b'). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

b. If the heat exchange is small, the following method is more convenient.

Extrapolate the curves T_a and T_f for values of $t < t_1$ by means of their tangents at $t = t_1$ and take the difference of the ordinates for

$$t = t_1 - \frac{O_1}{b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

See e.g. YX in Fig. 1, 2 and 5.

It is easily derived from equations (2) and (4) that in such a way the "ideal temperature increase" is obtained.

For k approaching to 0, t of (9) approaches to $\frac{1}{2}\ t_1$, which gives the rule commonly followed till now [2]), of extrapolating the fore- and after-period curves to the middle of the heating period.

As a second approximation, if k is small, this same rule may be followed, applying to the value of heat capacity c' found so [3]) the correction $\triangle c = c-c'$ calculated from

$$\frac{\triangle c}{c'} = -\frac{O_1 - \frac{1}{2}\,bt_1}{O}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

---

[1]) Small irregular fluctuations of the galvanometer are automatically cancelled with this method.

[2]) Cf. e.g. W. H. KEESOM and H. KAMERLINGH ONNES, These Proceedings **17**, 894, 1915. Comm. Leiden, N°. 143.

[3]) It should be remarked that, if the fore-period curve is not strictly straight, one ought to keep to the rule of extrapolating by their tangents not only the afterperiod curve, but also the (extrapolated) fore-period curve from the point $t = t_1$, and not the latter from $t = 0$. In practice these two procedures will, however, usually come to the same.

c. In applying the methods of correcting for heat exchange discussed to the experiments mentioned in § 2, we obtained for the ideal temperature increase in centimeters of galvanometer scale:

Experiment I:	Experiment II:
method *a*: 15.76 cm	method *a*: 6.38 cm
„ *a'*: 15.75 „	„ *a'*: 6.39 „
„ *b*: 15.85 „	„ *b*: 6.36 „

As a matter of fact the "planimeter method" described under *a* and *a'* will be preferred when heat exchange is rather great, the "extrapolation method" mentioned under *b* when heat exchange is rather small (Fig. 5 [1])).

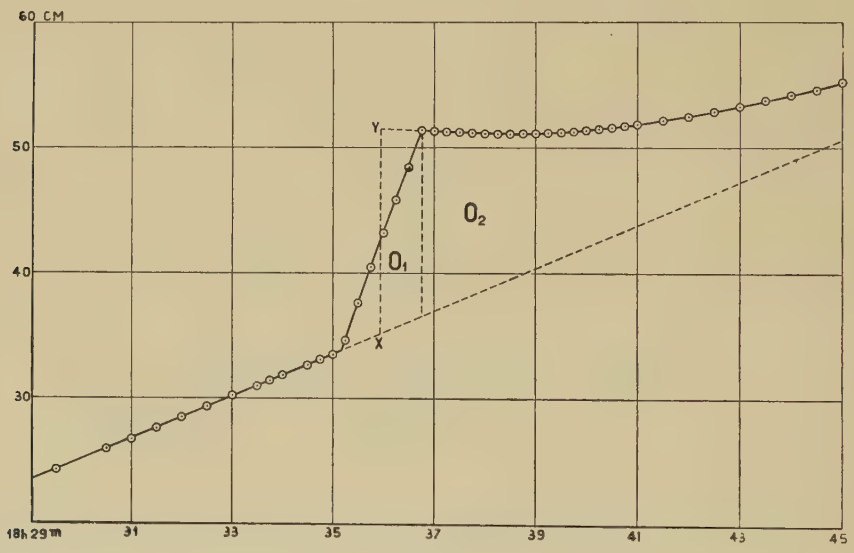

Fig. 5

The methods discussed have been tested for a number of cases in which measurements of the same heat capacity under different conditions of heat exchange were available [2]), and always proved to give satisfactory results.

Summary.

An accurate method was worked out for correcting for the heat exchange with the surroundings in measurements of very small heat capacities after NERNST and EUCKEN's method if thermal isolation is incomplete.

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[1]) The galvanometer readings belong to a series of measurements on silver, made Nov. 19th, 1931. The temperatures at the beginning and at the end of the heating were 2,928 and 3,130° K.

[2]) Cf. These Proceedings **35**, 143, 1932, Comm. Leiden N°. 219*b*, Tables I and II, where the temperature increases denoted by *p* were derived by the planimeter method.

Physics. — *Measurements of the specific heats of silver from 1.35 to 20.3° K.* By W. H. KEESOM and J. A. KOK. (Comm. N°. 219*d* from the Kamerlingh Onnes Laboratory at Leiden).

(Communicated at the meeting of April 2, 1932.)

§ 1. *Introduction.* These measurements are a continuation of the investigations on the specific heats of lead, bismuth, tin and zinc, which were made by one of us and J. N. VAN DEN ENDE [1]).

We chose silver, because we could expect from the heat capacity per cM^3, that at very low temperatures the heat capacity of the block to be used, could still be measured with sufficient accuracy.

§ 2. *Method.* We followed the method, described in Comm. N°. 203*d* and N°. 219*b*. For the calibration of the phosphorbronze-thermometer we refer to Comm. N°. 219*b*. The constantin-thermometer was once more calibrated in the liquid hydrogen range of temperature. The silver was supplied by the "Zilverfabriek" at Voorschoten. The purity was guaranteed to be at least 99.95 % [2]). The silverblock weighed 1185.70 g.

Though in these measurements the heat capacities were smaller than in the measurements of tin [3]), the vacuum proved to be so good, that we could use the method of extrapolating the temperature curves before and after the heating, to the middle of the heating period (Fig. 1) [4]).

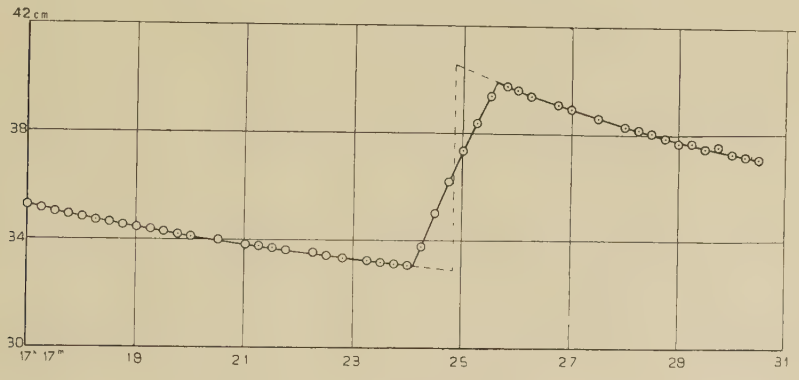

Fig. 1

[1]) W. H. KEESOM and J. N. VAN DEN ENDE. These Proceedings **33**, 243, 1930; Comm. Leiden No. 203*d* and These Proceedings **35**, 143, 1932, Comm. Leiden No 219*b*.

[2]) Chem. Cand. J. DROP was so kind as to check the silver by chemical analysis. He found an appreciably smaller amount of impurity.

[3]) These Proceedings **35**, 1932, 143, Comm. Leiden No. 219*b*.

[4]) In some cases extrapolation to the time indicated by equ. (9) of the preceding paper was necessary.

§ 3. *Results.* The results are given in table I and represented in Fig. 2.

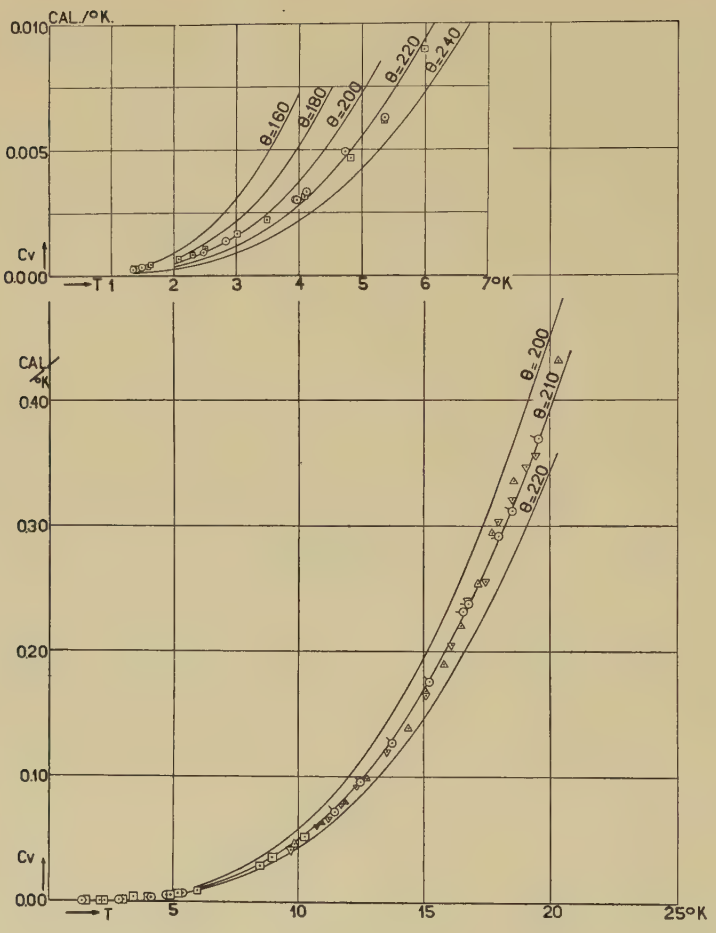

Fig. 2.

▽ Nov. 4th, 1931.

△ Nov. 10th, 1931.

⊡ Nov. 19th, 1931.

⊙ Nov. 26th, 1931.

⊙ A. EUCKEN, K. CLUSIUS and H. WOITINEK.

The points we found in the hydrogen range agreed well with those of EUCKEN, CLUSIUS and WOITINEK [1]).

[1]) A. EUCKEN, K. CLUSIUS and H. WOITINEK. Zs. f. anorg. u. allgem. Chemie, 203, 40, 1931.

TABLE I.

Atomic heat of silver								
N⁰.	Heat supplied cal.	Tempe-rature °K	Temp. change °K	Total heat capacity cal/°K	Heat cap. core cal/°K	Atomic heat silver cal/°K	θ	Resistance thermometer, measuring current
Nov. 4th 1931 (in solid/liquid hydrogen)								
Ia	0.1090	9.705	0.221	0.4933	0.0199	0.04307	214.2	constantin 1 mA.
b	0.1193	10.786	0.173	0.6894	0.0265	0.06031	212 8	
c	0.1835	11.180	0.241	0.7616	0.0293	0.06663	213.3	
d	0.3850	11.742	0.435	0.8849	0.0339	0.07743	213.6	
e	0.7848	12.345	0.743	1.0562	0.0391	0.09254	211.2	
f	1.2715	13.562	0.924	1.3761	0.0508	0.1206	212.2	
g	0.9336	15.110	0.496	1.8822	0.0690	0.1650	213.1	
h	0.8372	16.086	0.357	2.3450	0.0822	0.2059	211.0	
i	0.8556	16.732	0.311	2.7513	0.0930	0.2419	207.6	
j	0.9396	17.476	0.321	2.9272	0.1065	0.2566	212.5	
k	1.041	17.981	0.301	3.4592	0.1166	0.3041	206.4	
l	1.286	18.497	0.351	3.6632	0.1281	0.3216	208.3	
m	1.458	19.059	0.368	3.9611	0.1425	0.3474	209.1	
n	1.716	19.422	0.421	4.0767	0.1540	0.3569	211.1	
Nov. 10th 1931 (in solid/liquid hydrogen)								
Ia	0.3750	9.831	0.723	0.5187	0.0205	0.04533	213.5	constantin 1 mA.
b	0.4510	10.940	0.622	0.7251	0.0277	0.06345	212.2	
c	0.6431	11.862	0.705	0.9122	0.0348	0.07983	213.5	
d	0.9437	12.748	0.839	1.1248	0.0427	0.09845	213.9	
e	0.8713	13.759	0.592	1.4718	0.0487	0.1295	210.5	
f	1.329	16.062	0.576	2.3082	0.0811	0.2026	211.7	
IIa	1.178	14.387	0 742	1.5881	0.0598	0.1391	214.6	
b	1.373	15.085	0.712	1.9287	0.0685	0.1693	211.0	
c	1.652	15.817	0.760	2.1739	0.0782	0.1907	212.7	
d	1.772	16.459	0.705	2.5130	0.0882	0.2206	210.7	
e	2.371	17.160	0.821	2.8877	0.1008	0.2536	209.5	
f	2.346	17.812	0.699	3.3555	0.1138	0.2949	206.6	
g	2.584	18.586	0.677	3 8168	0.1297	0.3357	206.4	
h	3.288	19.439	0.780	4.2159	0.1545	0.3695	208.7	
i	4.055	20.314	0.820	4.9455	0.1849	0.4314	206.5	

TABLE I (*Continued*).

N°.	Heat supplied cal.	Temperature °K	Temp. change °K	Total heat capacity cal/°K	Heat cap. core cal/°K	Atomic heat cal/°K	θ	Resistance thermometer measuring current
Nov. 19th 1931 (in liquid helium)								
Ia	0.0009548	1.614	0.182	0.00525	0.00095	0.0003912	170.9	phosphor-bronze 0.4 mA.
b	0.001309	1.637	0.234	0.00559	0.00090	0.0004267	168.4	
IIa	0.001343	1.394	0.131	0.01025	0.00726	0.0002720	166.7	
b	0.001328	2.086	0.159	0.00835	0.00101	0.0006678	184.9	
c	0.002236	2.308	0.217	0.01030	0.00110	0.0008371	189.6	
d	0.003347	2.514	0.261	0.01282	0.00120	0.001057	191.2	
e	0.003722	3.029	0.190	0.01959	0.00149	0.001647	198.8	
f	0.002407	3.493	0.092	0.02613	0.00181	0.002213	207.5	
g	0.002906	3.944	0.082	0.03536	0.00218	0.003019	211.4	
h	0.004019	4.089	0.108	0.03721	0.00232	0.003174	215.5	
i	0.004414	4.820	0.081	0.05449	0.00323	0.004664	223.2	
j	0.008061	5.358	0.113	0.07133	0.00403	0.006123	226.9	
k	0.009558	5.984	0.092	0.10389	0.00525	0.008975	222.9	
l	0.2104	8.480	0.645	0.3262	0.01352	0.02848	215.2	constantin 1 mA.
m	0.1628	8.988	0.418	0.3895	0.01560	0.03401	214.9	
n	0.3757	10.275	0.627	0.5992	0.0229	0.05180	213.8	
o	0.3195	11.330	0.388	0.8235	0.0306	0.07214	210.7	
Nov. 26th 1931 (in liquid helium)								
Ia	0.0006950	1.353	0.080	0.00870	0.00601	0.0002447	167.5	phosphor-bronze 0.4 mA.
b	0.001046	1.402	0.108	0.00966	0.00669	0.0002703	168.0	
c	0.001492	1.492	0.195	0.00766	0.00392	0.0003403	165.6	
d	0.003315	2.474	0.288	0.01149	0.00118	0.0009380	195.9	
e	0.004097	2.837	0.247	0.01659	0.00137	0.001385	196.9	
f	0.01376	3.977	0.391	0.03519	0.00221	0.002992	213.7	
g	0.01090	4.122	0.281	0.03885	0.00236	0.003320	214.0	
h	0.01423	4.738	0.249	0.05713	0.00310	0.004916	215.7	
i	0.01468	5.365	0.191	0.07687	0.00403	0.006273	225.3	

The values of θ, represented in Fig. 3, show a maximum at 5.4° K ($\theta = 226$). At lower temperatures they become much smaller, till $\theta = 165$ at 1.35° K.

A similar decrease of values of θ with decreasing temperature, was

already observed in the investigations on the specific heats of zinc [1]) and mercury [2]).

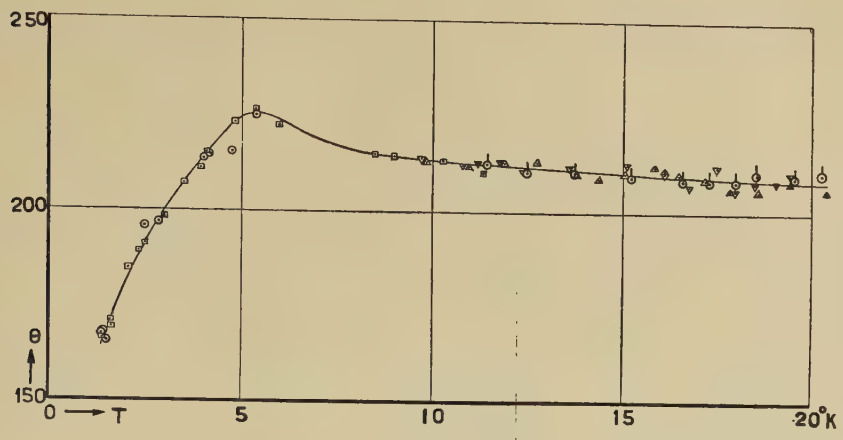

Fig. 3.

▽ Nov. 4th, 1931.
△ Nov. 10th, 1931.
⊡ Nov. 19th, 1931.
⊙ Nov. 26th, 1931.

⊙ A. EUCKEN, K. CLUSIUS and H. WOITINEK.

In table II values of θ are given, which have been read from Fig. 2. We also give interpolated values of the atomic heats calculated by means of those θ. It proves that below 6° K silver follows by no means a T^3-curve. We should rather be inclined to think of a T^2-curve, though it is not quite exactly this [3]).

It is noteworthy, that the curves of the atomic heats of zinc and silver intersect at 14° K in such way, that silver has larger atomic heats than zinc below that temperature.

The points between 1.35 and 1.55° K are not accurate, because in the

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[1]) W. H. KEESOM and J. N. VAN DEN ENDE, These Proceedings **35**, 143, 1932, Comm. Leiden No. 219*b*.

[2]) F. SIMON, Zs. physik. Chem. 107, 279, 1923. H. KAMERLINGH ONNES and G. HOLST, These Proceedings **17**, 760, 1914, Comm. Leiden N°. 142*c*, F. POLLITZER, Zs. f. Elektrochem. **17**, 5, 1911.

[3]) The rapid descent of the θ-curve for silver is surprising, the more so as for zinc the same behaviour has been found. This descent for both metals might be explained by a supplementary heat capacity of the block at 2—3° K. of 0.0026 cal/° K. At first sight one might be inclined to think of a layer of helium adsorbed to the surface of the block. We think this supposition not tenable, as the quantity of helium adsorbed ought to be about 6 times the quantity contained as gas in the core. This gas, for which conditions for adsorption are better than for the gas in the vacuum space, is, however, not adsorbed to a notorious degree, to judge from its liquefaction which occurs at a temperature agreeing with that estimated from its initial pressure.

region below 1.5° K the core has a somewhat larger heat capacity, caused by the evaporation of condensed helium.

We gladly express our thanks to phil. nat. cand. A. P. KEESOM for her valuable assistance in the measurements and calculations.

TABLE II.

Atomic heat of silver.
Smoothed values.

T °K	θ	Atomic heat cal/°K
1.35	165	0.000254
2	181	0.000626
3	200	0.00157
4	214	0.00303
5	225	0.00509
5.4	226	0.00634
6	224	0.00891
7	219	0.0151
8	216	0.0236
10	214	0.0475
12	213	0.0830
14	212	0.1336
16	211	0.2020
18	210	0.2898
20	209	0.3995

Summary.

We measured the atomic heats of silver between 1.35° K and 20.3° K. The results of these measurements are given in tables I and II.

The value of θ of silver is almost constant in the liquid/solid hydrogen range, it reaches a maximum at 5.4° K ($\theta = 226$) and decreases below this temperature to $\theta = 165$ at 1.35° K.

Physics. — *Ueber die spezifische Wärme des flüssigen Heliums.* Von W. H. KEESOM und K. CLUSIUS. Communication N°. 219e from the KAMERLINGH-ONNES Laboratory at Leiden.

(Communicated at the meeting of April 2, 1932.)

§ 1. *Einleitung.* Die spez. Wärme des flüssigen Heliums ist bereits Gegenstand einer Untersuchung gewesen. DANA und KAMERLINGH ONNES [1]) haben die spez. Wärmen beim Sättigungsdruck zwischen 4.05° und 2.61° K mitgeteilt und festgestellt, dass in diesem Temperaturbereich der Verlauf der Messdaten in erster Näherung durch eine lineare Funktion wiedergegeben werden kann.

Es war wünschenswert, unsere Kenntnisse über diesen Gegenstand zu erweitern und nach tieferen Temperaturen vorzudringen als es den genannten Forschern möglich war. Dazu gab besonders der Umstand Anlass, dass flüssiges Helium offenbar in zwei verschiedenen Zuständen existiert, die bei etwa 2.19° K ineinander überzugehen scheinen [2]).

Besonders dürfte man auch erwarten durch Messungen der spezifischen Wärme unter höherem Druck die dadurch verursachte Verschiebung des Umwandlungspunktes messend verfolgen zu können. Zu dem Zweck wurde das Kalorimetergefäss so konstruiert dass es die geplanten Drucke auszuhalten vermag.

Äussere Umstände haben veranlasst, dass bis jetzt Messungen der spezifischen Wärme bei höheren Drucken noch nicht haben stattfinden können. Dagegen hat der Verlauf der Umwandlungskurve aus bei verschiedenen Drucken aufgenommenen Abkühlungskurven genügend festgelegt werden können. Die in dieser Hinsicht gewonnenen Daten sind schon publiziert worden [3]).

Wir hatten auch gehofft die bezüglich der spezifischen Wärmen unter Sättigungsdruck erhaltenen Daten noch durch weitere Messungen zu vervollständigen. Weil diese geplante Fortsetzung der Arbeit aber jedesmal verschoben werden musste, glauben wir jetzt die Veröffentlichung nicht länger aufschieben zu dürfen.

§ 2. *Beschreibung der Apparatur.* Fig. 1 vermittelt eine Anschauung von den wesentlichsten Teilen der Apparatur, bei deren Aufstellung die in

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[1]) L. I. DANA and H. KAMERLINGH ONNES. These Proceedings, **29**, 1061, 1926; Comm. Leiden N°. 179*d*.

[2]) W. H. KEESOM und M. WOLFKE. These Proceedings, **31**, 90. 1928; Comm. Leiden N°. 190*b*. Die in dieser Veröffentlichung angegebene Temperatur von 2.30° K. ist nach der Temperaturskala von W. H. KEESOM, SOPHUS WEBER und G. SCHMIDT, These Proceedings, **32**, 1314, 1929; Comm. Leiden N°. 202*c*, geändert worden.

[3]) These Proceedings **34**, 605, 1931; Comm. Leiden N°. 216*b*.

diesem Institut gemachten Erfahrungen über die Messung spez. Wärmen bei Heliumtemperaturen nutzbringend verwendet wurden[1]). In einem Heliumkryostaten ist das Kalorimeter *A* vom einem Messingzylinder *B* hochvakuumdicht umschlossen. Ein nach oben weiter werdendes Neusilberrohr *N* gestattet, den Raum zwischen dem Messingmantel und dem Kalorimeter nach Bedarf zu evakuieren oder mit etwas Heliumgas zu beschicken, um den Temperaturausgleich mit dem Bad zu ermöglichen. Die Verwendung des Metallmantels bietet für das Kalorimeter den denkbar besten Schutz gegen Einstrahlung. Um auch die von oben her durch das Neusilberrohr einfallende Energie möglichst abzuschwächen, war an der Uebergangstelle zum weiteren Rohr ein Metallschirm *S* angelötet, der vom Bade her ebenfalls auf tiefe Temperatur gekühlt wurde. Die Entleerung des Messraumes erfolgte mittels einer dreistufigen Gaedeschen Stahlpumpe, die durch ein Glasrohr von 50 mm Durchmesser mit dem oberen Ende des Neusilberrohrs verbunden war. Das Kalorimeter selbst besteht aus zwei Teilen: dem einschraubbaren Kern, der die Organe zur Zuführung der Energie und zur Temperaturmessung trägt, und dem eigentlichen Kalorimetergefäss, das zur Aufnahme des flüssigen Heliums dient.

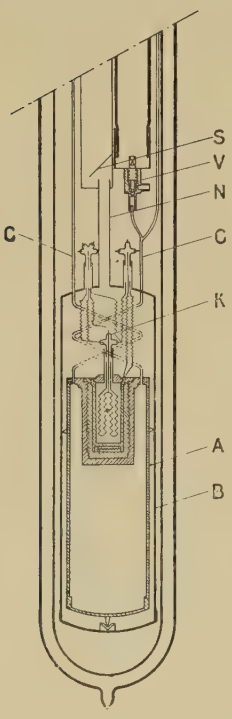

Fig. 1.

Der Kern weist dieselben Konstruktionsmerkmale auf, wie der entsprechende von KEESOM und VAN DEN ENDE benutzte Apparatenteil. Doch war noch in zweierlei Hinsicht verbessert; einmal kam nämlich zur Temperaturmessung das im vorliegenden Falle vorzüglich geeignete Phosphorbronzethermometer erstmalig zur Anwendung[2]), das wahlweise mit einem gealterten Konstantanthermometer benutzt werden konnte und wieder in einer Heliumatmosphäre hing. Ausserdem wurde die Durchführung der Zuleitung zu den Thermometerdrähten durch ein zierliches Glaskreuz *K* vorgenommen, was gegenüber der früher verwendeten Anordnung nicht nur eine wesentliche Platzersparnis, sondern vor allem einen schnellen Temperaturausgleich in diesem am Kern notwendigen Anhängsel sichert.

Das Kalorimeter besteht aus 1 mm dickem Kupferblech und hat ein Gewicht von 180.9 g. Es wird im Messingmantel mit Hilfe dreier stählerner Zentrierspitzen in seinem oberen Drittel und einer Fussspitze in einer definierten Lage gehalten. Die Fussspitze ruht dabei in einem Glashütchen, das am Boden des Messingmantels befestigt ist. Zum Kalorimeter führen

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[1]) W. H. KEESOM und J. N. VAN DEN ENDE. These Proceedings **33**, 243, 1930; Comm. Leiden N⁰. 203*d*.

[2]) W. H. KEESOM und J. N. VAN DEN ENDE. These Proceedings **32**, 1171, 1929; Comm. Leiden N⁰. 203*c*.

zwei Contracidkapillaren C von etwa 0.8 mm äusserem Durchmesser, von denen die eine über ein Ventil mit der Hochdruckleitung des Heliumkompressors und die andere mit einem im flüssigen Helium liegenden Absperrventil V [1]) verbunden ist. Unterhalb dieses Ventils führt eine Zweigleitung zu einem Präzisionsmanometer; das Kalorimeter selbst war auf einen Druck von etwa 50 atm. geprüft. Die Kapillaren sind gasdicht durch den Neusilber-Deckel des Messinggefässes geführt und im Kalorimeter eingelötet, nachdem sie zur Verringerung der Wärmeübertragung zwischen Bad und Kalorimeter noch eine kreisförmige Biegung erfahren haben. Im Deckel sind noch zwei Glaskreuze von ähnlicher Konstruktion wie das beim Kern verwandte mittels eingeschmolzener Nickelstahlröhrchen eingelötet, die zur Durchführung der Heizzuleitungen und der Potential- und Stromleitungsdrähte für die Temperaturmessung dienen.

Zur Füllung des Kalorimeters wurde das Heliumbad unter vermindertem Druck sieden gelassen. Nachdem alle Metallteile auf die entsprechende niedrige Temperatur abgekühlt waren und durch Oeffnen des Absperrventils die Verbindung mit dem gut evakuierten Kalorimeter hergestellt war, wurde jetzt der Druck über der Heliumoberfläche plötzlich auf 1 Atmosphäre erhöht. Man konnte dann beobachten, dass der Heliumspiegel rasch zu fallen begann und nach etwa 30 Sekunden ruckartig zum Stehen kam: das flüssige Helium war dann durch die engen Kapillaren durchgepresst worden und erfüllte das Kalorimeter. Um ganz sicher zu sein, dass die Füllung vollständig war, konnte man jetzt nach dem Schliessen des Absperrventils vom Kompressor her ein wenig Ueberdruck (ca. 2 Atm.) auf das Helium geben und beobachten, ob dass Manometer an der anderen Kapillare sofort ansprach. Dies war stets der Fall. Die nun folgende Entspannung auf den Sättigungsdruck wurde unter genauer Beobachtung der Kalorimetertemperatur vorgenommen und diese im endgültigen Augenblick des Schliessens der Ventile ermittelt.

Das Evakuieren bereitete recht grosse Schwierigkeiten. Es ergab sich aber, dass sich, nach etwa 45 Minuten währendem Pumpen, während dessen die Badtemperatur dauernd so niedrig wie irgend angängig (etwa 1.3° K) gehalten wurde, mehr und mehr ein deutlich aufwärts gerichteter Temperaturgang des Kalorimeters einstellte. Das Vakuum war inzwischen ständig besser geworden (ca. 10^{-4} mm Hg); dabei war durch kurze Heizstösse das am Kalorimeter möglicherweise absorbierte Gas möglichst entfernt worden. Die Messungen konnten dann beginnen und ergaben bereits bei 1.5° K brauchbare und gut reproduzierbare Werte.

§ 3. *Kalibration des Thermometers.* Die Thermometer wurden in flüssigem und festem Wasserstoff mittels zweier *Pt*-Widerstandsthermometer und im flüssigen Helium unter exakter Beobachtung des Dampfdruckes sorgfältig kalibriert, wobei zur Widerstandsmessung ein Potentio-

[1]) Vgl. etwa L. I. DANA und H. KAMERLINGH ONNES. These Proceedings **29**, 1051, 1926; Comm. Leiden N°. 179*c*.

meter nach DIESELHORST vortreffliche Dienste leistete. Da später nur Messungen im Gebiete des flüssigen Heliums und nur mit dem empfindlichen Phosphorbronzethermometer ausgeführt wurden, sei die Wiedergabe der Unterlagen hier auf diese Werte beschränkt.

TABELLE I.

Phosphorbronzewiderstand		Kern 1930 II
Beobachtungstag	Temp. °K	Widerstand Ω
17.X.1930.	4.233	22.0240
	3.591	21.1819
	2.919	20.3606
	2.516	19.9061
	2.042	19.4072
	1.524	18.9061
	1.158	18.4953
	1.473	18.8253
	1.831	19.2046
	2.149	19.5001
	2.597	19.9909
	2.917	20.3544
	3.299	20.8124
	3.586	21.1706
	4.013	21.7292
	4.351	22.1789
	4.287	22.0959
	4.219	21.9990
21.XI.1930.	4.220	22.0074
	2.245	19.6160
27.XI.1930.	4.163	21.9330

Zur Sicherheit wurde an jedem Messtage die eine und andere Temperatur nachgemessen und stets in Uebereinstimmung mit den früher erhaltenen Werten gefunden. Die Temperatur wurde von den neu ermit-

telten Dampfdruckkurven des flüssigen Heliums abgeleitet[1]). Der Temperaturverlauf des Widerstandes bei dem benutzten Thermometer war — wie schon früher gefunden — zwischen 1.15° K und 4.35° K nahezu linear. Der Benutzung dieses Thermometers ist vor allem die erhebliche Steigerung der Messgenauigkeit zu danken, die in der vorliegenden Arbeit erreicht wurde. Die Temperaturen wurden von einer in sehr grossem Masstab hergerichteten Zeichnung abgelesen, bei der alle gewonnenen Messpunkte vorzüglich auf einer Kurve lagen; es scheint jedoch zwischen den mit steigender und fallender Temperatur gemessenen Daten insofern ein kleiner Unterschied zu bestehen, als ersteren gegenüber den letzteren nahe der Fehlergrenze ein etwas grösserer Widerstandswert zugeordnet ist. Diese Störung dürfte jedoch sehr gering sein und macht in einem Falle maximal 0.010° gegenüber der als richtig angesehenen Kurve aus.

§ 4. *Heizenergie.* Die Messung geschah auf dem früher angegebenen Wege durch Beobachtung der Stromstärke I im Heizkreis, des Spannungsabfalls E am Heizwiderstand mittels eines Präzisionsampère-bezw. Voltmeters und durch geeignete Wahl der Heizzeit t, die nach der früher beschriebenen Methode[2]) durch eine Uhr mit Sekundenpendel festgelegt wurde. Der Heizwiderstand w betrug ca. 64.1 Ohm bei flüssiger Heliumtemperatur, sodass die im Kalorimeter bei einer Messung entwickelte Wärmemenge sich zu $\frac{E.I}{1+\frac{w}{w'}} \cdot \frac{t}{4.1824}$ cal berechnet. Durch das mit w' behaftete Glied wird der Stromverbrauch des Spannungsmessers berücksichtigt, wenn dessen Widerstand samt Zuleitung gerade w' beträgt. Diese Korrektur machte ca. 6 % im vorliegenden Falle aus.

§ 5. *Thermische und sonstige Eigenschaften des Kalorimeters.* Es ist nun notwendig, besonders auf einige wichtige thermische Eigenschaften des Kalorimeters kurz einzugehen. Am meisten steht dabei die Frage nach der Schnelligkeit und der Vollständigkeit des Temperaturausgleichs im Vordergrund des Interesses. Wie aus der hier gegebenen Beschreibung hervorgeht, war eine Vorrichtung zur Rührung des Kalorimeterinhalts, die sich auf elektromagnetischem Wege hätte bewirken lassen, nicht vorgesehen. Die Erfahrung lehrte, dass in der Tat der Temperaturausgleich nach etwa 4 Minuten unterhalb bis höchstens 6 Minuten oberhalb des Dichtemaximums vollzogen war. Die Fig. 2 zeigt eine typische Beobachtung mittlerer Güte über den Temperaturverlauf einer Messung. Die Abszisse gibt die Zeit, die Ordinate die Ablesung an der Kompensationsbank. Man erkennt den linearen Anstieg der Vorperiode, den starken

[1]) W. H. KEESOM, SOPHUS WEBER und G. NØRGAARD. These Proceedings **32**, 864, 1929; Comm. Leiden N°. 202*b* und W. H. KEESOM, SOPHUS WEBER und G. SCHMIDT l. c.

[2]) W. H. KEESOM und H. KAMERLINGH ONNES. These Proceedings, **17**, 894, 1915; Comm. Leiden N°. 143.

Temperatureffekt der Hauptperiode mit dem anschliessenden Absinken der Temperatur durch das Abströmen der Energie vom Kern in das Kalori-

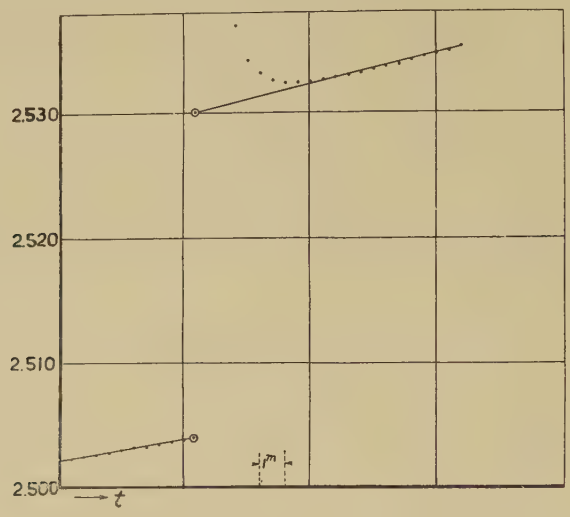

Fig. 2

meter, sowie die anschliessende Nachperiode. Man könnte im Zweifel sein, ob der Temperaturausgleich trotz der hervorragenden Temperatur-Leitfähigkeit des Kupfers genügend ist. Doch sprechen dafür folgende Umstände: Das Kalorimeter wird oben erwärmt. Bei Temperaturen unterhalb des Dichtemaximums senkt sich also die erhitzte Flüssigkeit in Schlieren in die kälteren Teile hinab und begünstigt den Temperaturausgleich durch mechanische Strömung. Oberhalb des Dichtemaximums schwimmt dagegen die spezifisch leichter gewordene Flüssigkeit auf den kälteren Teilen und der Temperaturausgleich kann nur durch Leitung der Wand erfolgen. Wäre der Ausgleich sehr mangelhaft, so würde nach der Heizung das Thermometer eine zu hohe Temperatur anzeigen, sodass eine zu kleine spezifische Wärme resultieren müsste. Nun zeigen aber die Ergebnisse dieser Arbeit gute Uebereinstimmung mit den Resultaten von DANA und KAMERLINGH ONNES innerhalb der Fehlergrenzen, bei deren Versuchen eine partielle Ueberhitzung infolge einer eingebauten Rührung nicht möglich war. Damit wird man zu der Annahme geführt, dass der beobachtete Temperaturausgleich bei unseren Versuchen tatsächlich genügend war und damit auch a fortiori bei Temperaturen unterhalb des Dichtemaximums ausreichte.

Trotz wiederholter Versuche erwies es sich als unmöglich, die Wärmekapazität des leeren Kalorimeters durch Messungen zu erfassen. Eine einfache Rechnung zeigt in der Tat, dass das Kalorimeter und der gleichfalls überwiegend aus Kupfer aufgebaute 77.9 g. wiegende Kern bei etwa 4° K nur einen Wärmeinhalt von 3.5×10^{-3} cal repräsentieren, falls das Debijesche T^3-Gesetz hier seine Gültigkeit behält. Bei etwa 2° K würden erst ca. 1600 kg Kupfer die gleiche Wärmekapazität wie das mit Helium

gefüllte Gefäss aufweisen. Wir haben es also mit einem idealen Kalorimeter zu tun, dessen Wärmekapazität praktisch gleich null zu setzen ist. Eine Fehlermöglichkeit verlangt jedoch kurze Diskussion: der mit Helium bei Zimmertemperatur unter 100 cm Druck[1]) gefüllte Kern würde einen gewissen Wärmeeffekt zeigen, wenn das Helium bei einer bestimmten Temperatur in ihm flüssig wäre, um bei der folgenden Heizperiode zu verdampfen. Man kann jedoch abschätzen, dass dieser Effekt erst bei 1.5° K und ungefähr 5 mm Druck eintreten könnte[2]).

Zur Mengenmessung des Heliums musste ausser der Fülltemperatur und der dadurch gegebenen Dichte noch das Volumen des Kalorimeters genau bekannt sein. Dieses wurde bei Zimmertemperatur durch eine exakte volumenometrische Messung mit Hilfe eines mit Quecksilber ausgewogenen Vergleichkölbchens von etwa gleichem Inhalt ermittelt und mit Hilfe des linearen Ausdehnungskoeffizienten des Kupfers[3]) auf Heliumtemperatur umgerechnet. Das Volumen ergab sich aus drei unabhängigen Messreihen bei 18° C zu 81.83 cm³ nach Anbringung aller Korrekturen mit einem wahrscheinlichen Fehler von $\pm$ 0.10 cm³. Aus diesem Werte erhält man durch Multiplikation mit dem Faktor 0.99045 das Volumen bei 4° K zu 81.05 ± 0.10 cm³.

Aus dieser Art der Mengenmessung geht hervor, dass die in den Kapillaren zurückbleibende Flüssigkeit nicht in Rechnung gestellt wurde. Wie eine Ueberschlagsrechnung zeigt, beträgt der so hervorgerufene Mengenfehler im ungünstigsten Falle 0.05 %, ist also gegenüber den durch zufällige Streuungen verursachten Fehlern gänzlich zu vernachlässigen.

§ 6. *Wärmeverluste und andere Korrekturen.* Wie aus der linearen Beschaffenheit der alle 30 Sekunden erfolgten Gangbeobachtungen hervorgeht, hat man anzunehmen, dass die Wärmeübergänge zur Umgebung regelmässig und unbeeinflusst durch die Heizperiode erfolgten, sodass die entsprechenden Korrekturen sich willkürfrei anbringen liessen.

Allerdings stellen die so erhaltenen Werte nicht immer direkt die spezifischen Wärmen beim Sättigungsdruck dar, da ja das Kalorimeter infolge der thermischen Kontraktion der Flüssigkeit meist nur teilweise gefüllt ist. Schliesst man aber durch Verwendung von Ueberdruck die Bildung der Dampfphase aus, so erhält man die spezifische Wärme C_v und keine Daten, aus denen C_s einfach ableitbar wäre. Wir haben daher den Dampfraum nach Massgabe der Dampfdruckmessungen von KEESOM, WEBER, NØRGAARD und SCHMIDT in entsprechender Weise korrigiert, wie es bei

[1]) Der Fülldruck hätte besser und ohne Beeinträchtigung der Wärmeübertragung kleiner sein können.

[2]) Spätere Messungen der Wärmekapazität des Heizkerns, vergl. W. H. KEESOM und J. N. VAN DEN ENDE, These Proceedings, **35**, 143, 1932, Comm. Leiden N⁰. 219*b*, Fig. 8, haben inzwischen ergeben, dass dieser Effekt aber nur etwa $^1/_{500}$ der Wärmekapazität des im Kalorimetergefäss enthaltenen flüssigen Heliums ausmacht.

[3]) W. H. KEESOM, F. P. G. A. J. VAN AGT und Miss A. F. J. JANSEN. These Proceedings **29**, 786, 1926; Comm. Leiden N⁰. 182*a*.

DANA und KAMERLINGH ONNES geschehen ist. Doch fiel letztere Korrektur nur bei der zweiten Messreihe ins Gewicht, da die erste mit einer Füllung in der Nähe des Dichtemaximums des Heliums unternommen wurde, sodass ein merklicher Dampfraum nicht entstand.

§ 7. *Verfahren bei den Versuchen:* Nachdem das Kalorimeter aufeinanderfolgend mit flüssiger Luft, flüssigem Wasserstoff und endlich flüssigem Helium abgekühlt worden war, wurde es in der beschriebenen Weise unter genauer Beobachtung der Temperatur gefüllt und so weit wie möglich abgekühlt. Die tiefste erreichbare Temperatur lag infolge der vielen in den Kryostaten führenden Metallteile nicht tiefer als 1.3° K.

Bei jedem Abkühlungsprozess wurde eine Abkühlungskurve aufgenommen, um das Verhalten der spezifischen Wärme schon rein qualitativ erfassen zu können. Nach dreiviertelstündigem Pumpen war dann ein genügendes Vakuum hergestellt, um die sukzessiven Aufheizungen zur Messung der spezifischen Wärme folgen zu lassen.

§ 8. *Ergebnisse und Diskussion.*

a. In Fig. 1 von Mitteilung N°. 216*b* wurde schon eine der erhaltenen Abkühlungskurven aufgetragen. Aus dem Aussehen der Kurve kann geschlossen werden, dass unterhalb von 2.19° K die spez. Wärme grösser sein muss als oberhalb. Wie ein Vergleich mit den anderen erhaltenen Resultaten zeigt, spiegelt die Abkühlungskurve in der Tat den Verlauf der spez. Wärme bis in alle Einzelheiten wieder.

Die Resultate von zwei Messtagen sind für die spez. Wärmen C_s auf Fig. 3 vereinigt und mit allen wesentlichen Unterlagen in den Tabellen II und III niedergelegt. Am meisten fällt sofort das starke Maximum bei 2.19° K auf. Während sämtliche bisher am Helium beobachteten Anomalien nur als relativ geringfügige Effekte in Erscheinung treten, zeigt sich

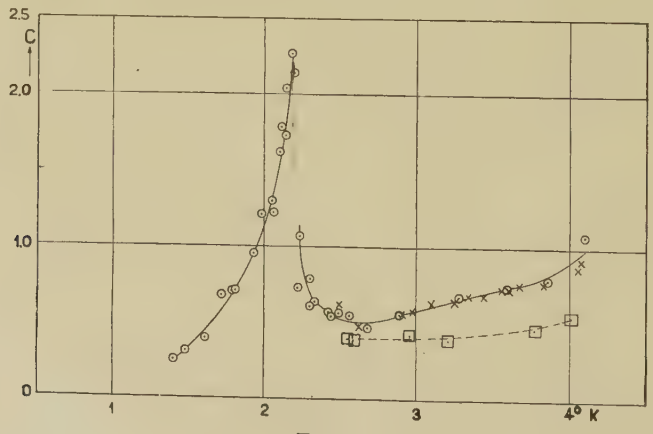

Fig. 3

⊡ C_v } KEESOM und CLUSIUS ⊙ C_s } KEESOM und CLUSIUS × DANA und KAMERLINGH ONNES.

TABELLE II.

Messung vom 4.12.30.

Versuchs-nummer	Heizstrom I in Milliampère	Heizzeit t in Sekunden	Heizspannung in Volt	Korrigierte sekundliche Energiezufuhr in Watt	Mittel-temperatur $\overline{T}$ °K.	Temperatur-differenz $\triangle T$ Grad K.	Wärme-kapazität des Systems Cal/°K.	Spez. Wärme C_s im Sättigungs-zustand Cal/°K. g
1	48.3	30	3.038	0.1423	1.979	0.072	14.160	1.212
2	48.3	8	3.046	0.1426	2.223	0.032	8.517	0.729
3	48.0	18	3.014	0.1403	2.298	0.085	7.096	0.608
4	48.2	24	3.022	0.1413	2.420	0.122	6.637	0.568
5	48.5	18	2.995	0.1418	1.720	0.077	7.915	0.678
6	48.4	24	3.026	0.1421	2.058	0.057	14.282	1.223
7	47.8	12	2.987	0.1385	2.114	0.019	20.883	1.788
8	48.0	20	3.003	0.1397	2.144	0.028	23.841	2.041
9	47.8	20	2.995	0.1389	2.176	0.025	26.522	2.271
10	48.3	30	3.026	0.1418	2.235	0.081	12.537	1.073
11	47.8	36	2.987	0.1385	2.440	0.187	6.365	0.545
12	48.0	36	3.022	0.1407	2.682	0.219	5.523	0.473

Anm.: Der Widerstand im Voltmeterkreis betrug 2000 Ohm.; der Kalorimeter enthielt 11.679 g Helium; die Fülltemperatur war 2.708° K.

TABELLE III.

Messung vom 11.12 30.

Versuchs-nummer	Heizstrom I in Milliampère	Heizzeit t in Sekunden	Heizspannung in Volt	Korrigierte sekundliche Energiezufuhr in Watt	Mittel-temperatur $\bar{T}$ °K.	Temperatur-differenz $\triangle T$ Grad K.	Wärme-kapazität des Systems Cal/°K.	Dampfraum-korrektur pro g Substanz	Spez. Wärme C_s im Sättigungs-zustand Cal/°K. g
1	43.6	12	2.685	0.1101	1.404	0.123	2.565	—	0.252
2	43.6	16	2.680	0.1098	1.478	0.133	3.142	—	0.308
3	43.0	20	2.668	0.1078	1.609	0.128	4.025	—	0.395
4	43.0	24	2.666	0.1077	1.790	0.086	7.184	—	0.705
5	43.2	32	2.678	0.1087	1.930	0.086	9.667	—	0.949
6	43.2	46	2.680	0.1088	2.047	0.090	13.288	—	1.304
7	42.8	34	2.646	0.1064	2.136	0.049	17.646	—	1.732
8	43.1	42	2.680	0.1084	2.192	0.050	21.788	—	2.139
9	43.0	42	2.666	0.1077	2.300	0.066	8.191	— 0.015	0.788
10	43.2	32	2.682	0.1089	2.487	0.140	5.947	— 0.019	0.565
11	43.3	72	2.682	0.1096	1.808	0.258	7.277	—	0.714
12	43.3	170	2.684	0.1092	2.098	0.273	16.492	—	1.619
13	43.3	42	2.690	0.1095	2.334	0.164	6.699	— 0.015	0.642
14	43.25	60	2.692	0.1094	2.564	0.272	5.767	— 0.019	0.546
15	43.25	76	2.694	0.1095	2.888	0.343	5.798	— 0.011	0.558
16	43.3	78	2.698	0.1098	3.280	0.296	6.913	+ 0.003	0.682
17	43.25	78	2.700	0.1098	3.588	0.276	7.411	+ 0.016	0.743
18	43.2	66	2.692	0.1093	3.865	0.225	7.659	+ 0.034	0.786
19	43.1	66	2.684	0.1087	4.098	0.167	10.266	+ 0.069	1.076

Anm.: Der Widerstand im Voltmeterkreise betrug 1000 Ohm; der Kalorimeter enthielt 10.188 g Helium; die Fülltemperatur war 4.245° K.

gerade die Messung der spez. Wärme als ausserordentlich geeignet, um einen Ueberblick über die hier waltenden energetischen Verhältnisse zu erlangen.

Wie man sieht, ist die Präzision bis zu den tiefsten Temperaturen vorzüglich, was vor allem der Anwendung des Phosphorbronzethermometers zuzuschreiben ist, da dessen vorzügliche, gleichmässige Empfindlichkeit noch Temperaturerhöhungen von 0.05 Grad auf etwa 1 % zu messen erlaubt. Dieser Umstand war für die genaue Ausmessung des Maximums besonders günstig. Die Messungen sehen wir auf etwa 3 % genau an; doch dürften die Resultate unterhalb 1.6° K mit dem doppelten Fehler versehen sein.

Einem steilen Anstieg bis zu Molwärmen von etwa 9.5 cal bei 2.19° K folgt ein plötzlicher Abfall auf etwa ein Drittel dieses Wertes, an den ein nahezu linearer Anstieg nach dem Durchlaufen eines deutlichen Minimums bei 2.65° K anschliesst. Die Messungen zwischen dem Maximum und dem Minimum zeigen auffallender Weise eine grössere Streuung, als man erwarten möchte. Man hat den Eindruck, als ob der jeweils gefundene Wert stark von Zufälligkeiten abhängig wäre. Oberhalb von 2.6° ist diese Unsicherheit wieder verschwunden.

Der Verlauf der spezifischen Wärme unterhalb 2.19° K zieht in hohem Maasse die Aufmerksamkeit auf sich. Von 1.4 bis 1.8° K kann die spezifische Wärme der gesättigten Flüssigkeit etwa durch 0.066 T^4 dargestellt werden. Oberhalb 1.8° K steigt sie steiler an. Es wäre vom grössten Interesse in diesem Gebiet die spezifische Wärme bei konstantem Volum zu messen.

In die Figur sind auch die nach den neuen Temperaturangaben umgerechneten Ergebnisse von DANA und KAMERLINGH ONNES eingetragen. Diese auf ganz anderem Wege erhaltenen Werte stimmen mit unseren Daten gut überein. Es ist interessant, dass z.B. der durch den tiefsten Messpunkt der genannten Forscher dokumentierte Anstieg tatsächlich vorhanden ist.

b. Von besonderem Interesse ist die Frage, ob der bei 2.19° K auftretende Effekt einer einfachen Phasenumwandlung zuzuschreiben ist oder nicht. Zu diesem Zwecke wurden dem im Vakuum befindlichen Kalorimeter stossweise sehr kleine Energiemengen unter gleichzeitiger Beobachtung der Temperatur zugeführt[1]). Das Ergebnis war ganz eindeutig, dass jeder Energiezufuhr stets eine Temperaturerhöhung gefolgt war. Diese wurde zwar in der Nähe von 2.19° sehr klein und darüber hinaus wieder grösser, blieb aber stets *endlich*. Daraus folgt, dass hier ein mit merklicher Umwandlungswärme behafteter eigentlicher Umwandlungspunkt im Sinne des Gibbs'schen Phasengesetzes *nicht* existiert.

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[1]) Vergl. die Messungen 7, 8, 9 vom 4.12.1930 (tab. II) und 6, 7, 8, 9 vom 11.12.1930 (tab. III). Ausserdem wurde bei einem Vorversuch das Maximum der spez. Wärme durch etwa noch 10 mal kleinere Heizstösse durchmessen und stets eine Temperaturerhöhung festgestellt.

Wir haben noch auf eine andere Weise unseren Schluss, dass bei 2.19° K keine merkliche Umwandlungswärme auftreten kann, zu erhärten gesucht. Misst man nämlich eine spez. Wärme über das Maximum in einem grossen Intervall fort, so muss der so erhaltene Wert mit dem durch graphische Integration über das gleiche Temperaturintervall erhaltenen Ergebnis übereinstimmen, falls keine merkliche Umwandlungswärme vorhanden ist. Der Versuch fällt so aus, dass zwischen 1.961 und 2.234° ein Wärmeinhalt von 0.442 cal/gramm gefunden wird, während die graphische Integration 0.441 cal/gramm ergibt, wie man es nach unsern vorher geschilderten Versuchen erwarten musste.

Obwohl also eine mit einem thermischen Effekt verbundene sprungweise Umwandlung nicht vorzuliegen scheint, so deutet doch das äusserst scharfe Maximum in der Kurve der spezifischen Wärme darauf hin, dass die vorliegende Erscheinung sich in der Hauptsache in einem sehr engen Temperaturintervall zusammendrängt. Diesem entspricht die Tatsache dass verschiedene Eigenschaften des flüssigen Heliums eine Aenderung erfahren [1]), die einem Sprung sehr ähnlich ist. In dem Sinne möchten wir den beobachteten Effekt noch immer als eine Umwandlung von einem Zustand II in einen Zustand I ansprechen.

c. Wenn im Vorangehenden auch das Wesen der Umwandlung näher geklärt worden ist, so muss man doch zugeben, dass uns ihre inneren Ursachen noch vollständig verborgen sind. Es scheint nicht sehr wahrscheinlich, einen einfachen Assoziationseffekt oder ähnliches annehmen zu dürfen. Analoge Erscheinungen, wie sie hier das flüssige Helium aufweist, sind bei gewissen festen Körpern, wie den Ammoniumsalzen [2]), festen Halogenwasserstoffen [3]) und dem Methan [4]) beobachtet worden [5]). Hier treten innere Umwandlungen auf, die nicht scharf an eine Temperatur gebunden, sondern eben über einen grösseren Temperaturbereich verstreut sind. PAULING [6]) hat eine Deutung dieses Verhaltens für gewisse Fälle in der Möglichkeit gesehen, dass bei sinkender Temperatur die Moleküle oder wenigstens Molekülbruchstücke, die zunächst im Gitter ungehinderte Drehbarkeit zeigen können, ihre Rotationsfreiheitsgrade nach und nach zugunsten von Oszillationsfrequenzen einbüssen. Wenn auch der Annahme von Rotationen beim Helium keine Bedeutung zukommt, so scheint eine innere Verwandschaft des beim Helium vorliegenden Effektes mit den in den festen Körpern aufgefundenen Anomalien insofern zu bestehen, als in der Flüssigkeit die oberhalb und unterhalb 2.19° K vorliegenden Zustände einen energetischen Unterschied aufweisen. Jedenfalls zeigt der

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[1]) Vergl. W. H. KEESOM und M. WOLFKE. These Proceedings **31**, 90, 1928; Comm. Leiden N⁰. 190*b*.

[2]) F. SIMON, CL. VON SIMON und M. RUHEMANN. Z. f. phys. Chem. **129**, 339, 1927.

[3]) A. EUCKEN und E. KARWAT. Z. physik. Chem. **112**, 467, 1924.

[4]) K. CLUSIUS. Z. physik. Chem. (B) **3**, 41, 1929.

[5]) Ein entsprechende Verhalten zeigen auch die Ferromagnetika am CURIE-punkt.

[6]) L. PAULING. Phys. Rev. **36**, 430, 1930.

TABELLE IV.

Versuchs-nummer	g Helium im Kalorimeter	Konzentration Mol/Liter	Heizstrom I in Milli-ampère	t Heizzeit im Sekunden	Heizspannung in Volt	Mittel-temperatur $\overline{T}$ °K.	Temperatur-differenz $\triangle T$ Grad K.	Wärme-kapazität des Systems Cal/°K.	Spec. Wärme C_v Cal/°K. g
4.12.30 1	11.679	36.02	48.3	36	3.030	2.960°	0.248	4.92	0.421
18.12.30 2	12.98	40.0	47.3	30	2.924	2.553	0.179	5.21	0.401
3	12.98	40.0	47.0	50	2.920	2.956	0.291	5.30	0.408
4	13.12	40.5	46.9	36	2.904	2.588	0.214	5.15	0.392
5	13.12	40.5	47.4	48	2.928	3.213	0.291	5.15	0.392
6	13.12	40.5	46.3	56	2.878	3.781	0.271	6.17	0.470
7	11.92	36.8	46.7	36	2.898	4.007	0.167	6.55	0.549

Anm.: Beim Versuch 1 betrug der Widerstand im Voltmeterkreis 2000 Ohm; bei den übrigen Versuchen 1000 Ohm.

hier vorliegende Effekt aufs Deutlichste die Notwendigkeit, auch an prinzipiell sehr einfach strukturierten Körpern Messungen bei extrem tiefen Temperaturen vorzunehmen.

d. Wir können unsere Ergebnisse noch durch einige Daten ergänzen, die wir für die spez. Wärme C_v des flüssigen Heliums oberhalb 2.5° K erhalten haben. Diese Messungen sind in Fig. 3 und Tabelle IV ebenfalls mit eingetragen und infolge einer gewissen Unsicherheit der Mengenmessung nicht so zuverlässig wie die C_s-Messungen. Die Mengenmessung geschah in der Weise, dass die Kompressibilität des Heliums bei 2.71° K ermittelt [1]) und mittels des Fülldruckes die zusätzliche Menge Helium bei dieser Temperatur abgeschätzt wurde. Die C_v-Werte, deren Druckabhängigkeit nicht berücksichtigt werden konnte, steigen mit der Temperatur schwach an und zeigen somit ein ganz entsprechendes Verhalten wie die C_v-Werte des Wasserstoffs im Flüssigkeitsgebiet [2]). Helium scheint ausser Wasserstoff die einzige Flüssigkeit zu sein, bei der ein solcher Quanteneffekt noch nachweisbar ist. Wenigstens wurde bei Neon [3]) ein Anstieg der C_v-Werte dicht oberhalb des Schmelzpunktes nicht mehr beobachtet.

Zusammenfassung.

Die spezifische Wärme flüssigen Heliums unter Sättigungsdruck wurde gemessen zwischen 1.4 und 4.1° K. Von 1.4° K an steigt die Kurve der spezifischen Wärmen steil an, bis sie bei 2.19° K ein scharfes Maximum (Atomwärme etwa 9 cal) zeigt, dann schnell zu einem flachen Minimum bei etwa 2.6° K abfällt um nachher, in Uebereinstimmung mit dem Befunde von DANA und KAMERLINGH ONNES, leicht anzuwachsen.

Diese Messungen wurden durch einige Beobachtungen der spezifischen Wärme bei konstantem Volum zwischen 2.5 und 4.0° K ergänzt.

[1]) Siehe die folgende Abhandlung.

[2]) A. EUCKEN. Verhandl. d. D. phys. Ges. **18**, 4, 1916. W. H. KEESOM und H. KAMERLINGH ONNES, These Proceedings **20**, 1000, 1918; Comm. Leiden N°. 153*a*.

[3]) K. CLUSIUS. Z.f. phys. Chem. (B) **4**, 1, 1929.

Physics. — *Eine vorläufige Bestimmung der Kompressibilität des flüssigen Heliums bei 2.7° K.* Von W. H. KEESOM und K. CLUSIUS. Communication N°. 219*f* from the KAMERLINGH-ONNES-Laboratory at Leiden.

(Communicated at the meeting of April 2, 1932.)

In der vorangehenden Abhandlung sind einige Daten über die spezifische Wärme C_v des flüssigen Heliums mitgeteilt worden. Um den Füllungsgrad des Kalorimeters unter Druck ermitteln zu können, war die

Bestimmung der Kompressibilität des Heliums bei wenigstens einer Temperatur erforderlich. Die Messungen machten keinerlei Umstände, da sie mit der bereits vorhandenen Apparatur ohne weiteres durchführbar waren. Es war nur nötig, das Kalorimeter bei konstanter Temperatur mit einem bekannten Ueberdruck zu füllen und die bei der Entspannung um einen bestimmten Druck austretende Substanzmenge zu ermitteln. Da die Dichte des Heliums unter dem Sättigungsdruck und der Inhalt des Kalorimeters bekannt sind, dessen Volumenänderungen bei den hier auftretenden kleinen Drucken gänzlich zu vernachlässigen sind, liegen alle zur Berechnung nötigen Daten vor [1]).

Die Entspannung erfolgte in einem evakuierten Glaskolben von etwa 4 Liter Inhalt, dessen Volumen durch Auswiegen mit Wasser bis zur Hahnbohrung exakt bestimmt war, und der sich während des Versuches in einem Wasserbad von bekannter Temperatur befand. Das zusätzliche zwischen dem Entspannungsventil und dem genannten Hahn befindliche Volumen wurde volumenometrisch festgestellt und berücksichtigt; diese Korrektur betrug nur 0.4 %. Ferner musste das schädliche Volumen des Hochdruckmanometers und seiner Zuleitung in Rechnung gestellt werden, da ein Teil des in diesen Leitungen enthaltenen Gases an der Expansion in den Kolben teilnahm. Diese Korrektur beeinflusste das Endergebnis um 2.8 bis 3.0 %. Als Manometer am Kolben war ein *U*-Rohr von 15 mm lichter Weite und Barometerhöhe vorgesehen, bei dem der Druck in dem mit der Apparatur verbundenen Schenkel durch Spiegelung an einem eingeschmolzenen Dorn eingestellt wurde, sodass der schädliche Raum stets die gleiche Grösse behielt.

Der Kompressibilitätskoeffizient χ ergibt sich einfach zu

$$\frac{1}{n_T} \cdot \frac{\triangle n_T}{\triangle p} = \chi,$$

wenn mit dem Differenzenquotienten die Aenderung der Molzahl bei der Entspannung und mit n_T die Molmenge beim jeweiligen Druck und der Temperatur T bezeichnet wird.

Die beiden bei 2.71° K durchgeführten Versuche ergaben folgende Werte:

TABELLE.

Die Kompressibilität flüssigen Heliums.

n_T	$p_2 - p_2 = \triangle p$ in kg/cm²	$\triangle n_T$	$\bar{p}$	$\chi \cdot 10^3$ cm²/kg.
2.9825	9.95—7.70 = 2.25	0.04820	8.87	7.18
2.970_0	7.70—4.95 = 2.75	0.0670_2	6.52	8.21

[1]) Vgl. z.B. A. EUCKEN. Verh. d. D. phys. Ges. 18, 4. 916.

Das Ergebnis ist insofern interessant, als flüssiges Helium die grösste aller bisher bei Flüssigkeiten gemessenen Kompressibilitäten aufweist. Ueber die Zusammendrückbarkeit flüssiger Gase ist bisher fast nichts bekannt. Lediglich beim Wasserstoff fand EUCKEN [1]) am Siedepunkt einen Wert, der etwa 4 mal kleiner als der hier beim Helium unterhalb des Siedepunktes erhaltene ist. Bei unseren Versuchen kommt die grosse Druckabhängigkeit der Kompressibilität deutlich zum Ausdruck. Extrapoliert man die von uns erhaltenen Werte linear auf den Sättigungsdruck, so erhält man ein χ von $11{,}19 \cdot 10^{-3}$ cm²/kg. Dieser Wert stellt offenbar einen unteren Grenzwert dar, da ja die lineare Extrapolation sicherlich nicht exakt zutreffend ist.

Wir können den so erhaltenen Wert mit Hilfe der in der vorangehenden Arbeit bestimmten spez. Wärmen prüfen. Es ist nämlich

$$\chi = T \frac{V \alpha^2}{C_p - C_v};$$

wir erhalten unter Einsetzung der zu 2.71° gehörigen Werte (wobei die Identifizierung von C_s mit C_p statthaft ist) und Umrechnung der spez. Wärmen in Molwärmen und Kilogrammcentimeter

$$\chi = \frac{2.71 \times 27.7 \times (0.0499)^2}{0.09 \times 4 \times 42.69} = 12.2 \cdot 10^{-3} \text{ cm}^2/\text{kg},$$

einen Wert, der noch etwas grösser als der experimentell gefundene ist, was nach dem Gesagten auch zu erwarten war.

Zusammenfassung.

Eine vorläufige Bestimmung der Kompressibilität von flüssigem Helium bei 2.71° K und Drucken von etwa 5 bis 10 kg/cm² lieferte Werte die alle bisher bei Flüssigkeiten gemessenen Kompressibilitäten beträchtlich überschreiten. Der bis kleine Drucke extrapolierte Wert der Kompressibilität stimmt mit dem aus Ausdehnungskoeffizient und Unterschied der spezifischen Wärmen bei konstantem Druck und bei konstantem Volum errechneten Wert befriedigend überein.

[1]) A. EUCKEN l.c.

Physics. —*The conduction of heat of lead-thallium at low temperatures.* By W. J. DE HAAS and H. BREMMER. (Communication N°. 220*c* from the Kamerlingh Onnes laboratory Leyden.)

(Communicated at the meeting of April 2, 1932.)

§ 1. After having investigated the thermal conductivity of the pure supraconductors lead, tin and indium at low temperatures [1]) we now used the same apparatus to determine the change of the thermal resistance with the temperature for the alloy $Pb\,Tl_2$. This alloy was chosen, because it is a supraconductor (transition point 4°.09 K), consisting of two supraconductors (transition point *Tl* 2°.37 K, transition point *Pb* 7°.2 K). We intended to find out, whether here also a connexion exists between supraconductivity and conduction of heat, as we have found for pure indium, lead and pure tin. Moreover the transition point of the alloy (4°.09 K) lies favourably in the temperature region of liquid helium.

For the measurements we used a short thick rod long 9 mm, thick 7.4 mm (which had been annealed during 180 hours slightly below the melting point). We chose these dimensions in order to obtain at the low temperatures a thermal resistance of the same order as in the measurements with the pure metals. A rod of the alloy of the same dimensions as of those of the pure metals would have had a much greater thermal resistance, so that a stationary temperature difference between the extremities of the rod would only have been reached after a long time.

For our measurements in the neighbourhood of the melting point of ice the described form of the little rod had still another advantage. In other cases at such temperatures the loss of heat by radiation within the apparatus becomes very large. As the rod was short and thick the conditions were now better. In these measurements the ratio of the heat passing through the rod by conduction to the heat radiated by the bulb of the gas thermometer and the heating body was about 5 : 1. By an estimation we found, that the radiation from the surface of the rod might be neglected.

Tables I and II give the results of the measurements, the thermal resistance (w) in Watt^{-1} at different temperatures.

Table II, which gives the measurements in the helium region, also contains the (longitudinal) magnetic field (H) in Gauss.

In fig. 1 and 2 the w-T-curves have been plotted. Above 4°.09 K the thermal resistance evidently increases, when the temperature is lowered. This is also the case probably at room temperature, so that a minimum if it exists, may be expected above room temperature.

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[1]) These Proceedings **34**, 325, 1931, **35**, p. 131, 1932, Comm. Leyden, 214*d* and 220*b*.

TABLE I

T °K.	W Watt^{-1}
276	15.6
95	22.0
82	24.9
20.9	38.7
18.2	42.7
16.2	46.7
15.1	49.2

TABLE II

T	H Gauss	W Watt^{-1}	T	H Gauss	W Watt^{-1}
5.69	0	108	3.17	642	189
5.69	749	107	3.15[5]	481	174
4.34	0	153	3.12	0	133
3.88	481	161	2.61	0	132
3.88	749	164	2.21	481	157
3.87	0	153	2.17	0	120
3.84	0	151	2.02	749	191
3.66	642	175	2.00	481	168
3.66	835	179	1.97	0	133
3.65	481	170	1.97	214	142
3.63	0	142			

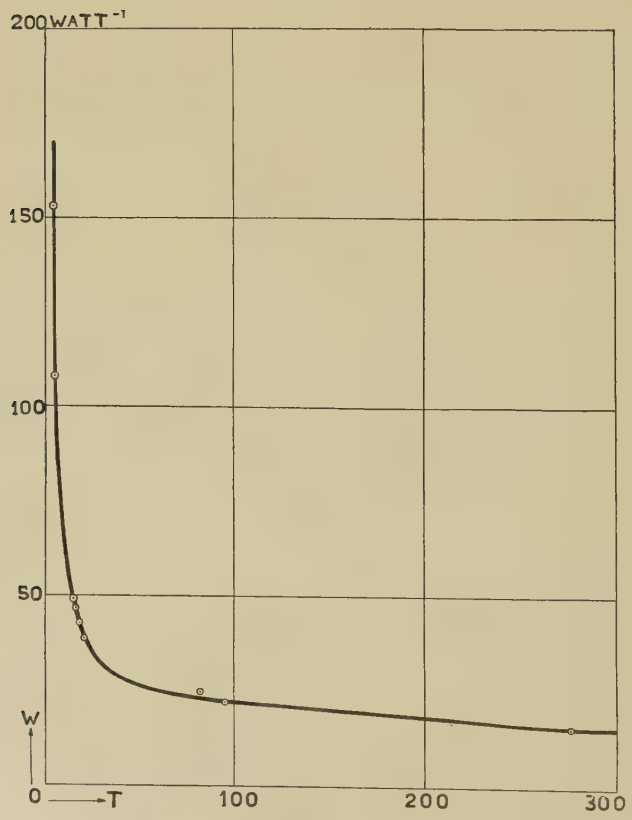

Fig. 1

On the whole alloys are known as well with thermal resistances that increase as with such that decrease when the temperature is lowered.

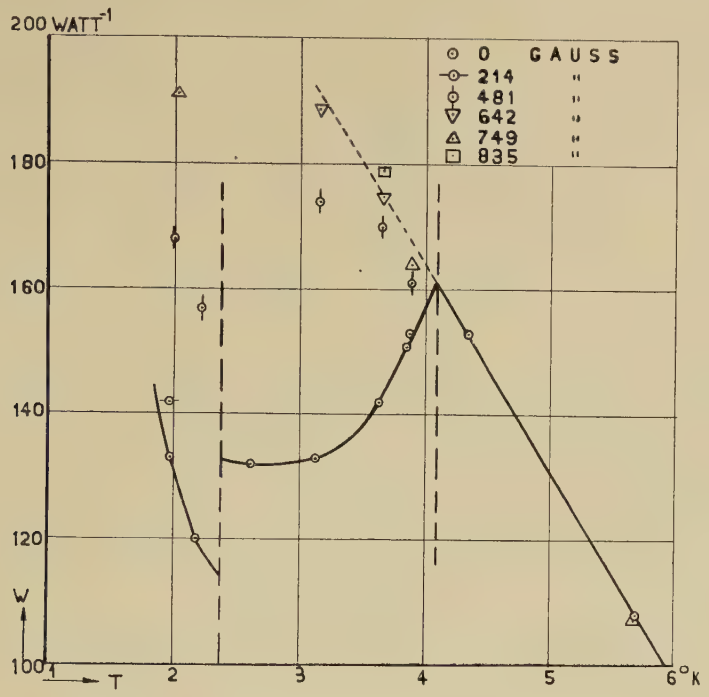

Fig. 2

§ 2. Interesting is the form of the curve in the region of liquid helium. Let us first consider in fig. 2 the points measured without a magnetic field. We see, that above the transition point 4°.09 of $Pb\,Tl_2$ the thermal resistance increases with sinking temperature in the same way as in the measurements of the pure metals. For these we found namely at a definite temperature a minimum of the thermal resistance, which may be due to impurities.

In the case of $Pb\,Tl_2$ we see that the normal increase of the thermal resistance is disturbed. At 4°.09 K the w-T-curve shows a change of direction; the thermal resistance decreases even. At the transition point of Tl 2°.37 another discontinuity occurs. Further downward the resistance increases in the usual way.

Should the discontinuity at 2°.37 be due to the occurrence of free thallium, than the thallium must show a great change in thermal resistance at its electrical transition point.

The change of direction at 4°.09 must be a property of the alloy lead-thallium.

The magnetic field is always found to increase the thermal resistance, except at 5°.69 where a very small decrease is found which is of the same order of magnitude as the accuracy of the measurements. Perhaps this has

something to do with the fact, that one of the components of the alloy is lead, (transition point 7°.2) and that we measured here in a magnetic field higher than the threshold value of lead.

At hydrogen temperatures we could not detect any change in the same field, though the accuracy of the measurements was greater here.

At all temperatures below 4.°09 K we see a strong increase of the thermal resistance in magnetic fields.

The phenomena in this temperature region are illustrated by figures 3, 4

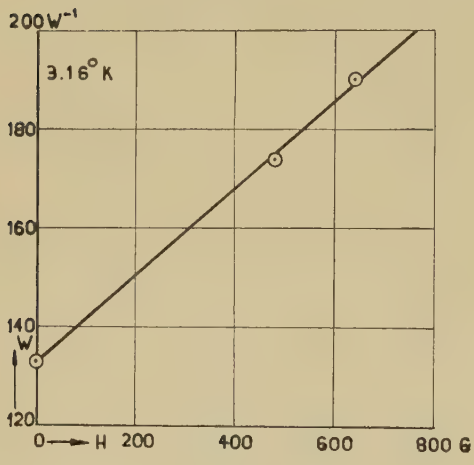

Fig. 3

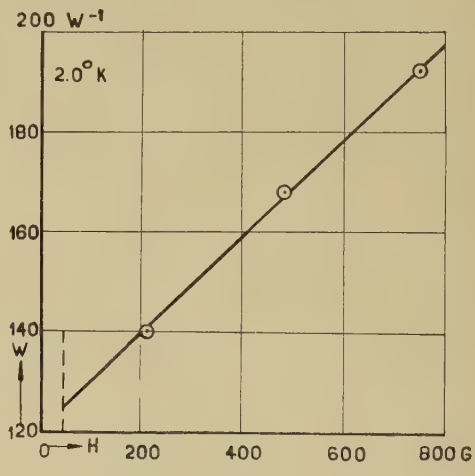

Fig. 4

and 5, where for a definite temperature w has been plotted as a function of the magnetic field H. Most times the temperatures, at which the measurements in the different magnetic fields were made, are not quite the same, as is seen from table 2. We then estimated how great w would have been at the slightly different temperature, to which the figure refers.

To begin with fig. 3. Here we have only to do with magnetic fields lower than the field, in which for lead-thallium the electrical resistance begins to come back and which we shall call the initial field. We are below the transition point of lead-thallium and above that of thallium.

The curve shows a linear increase of w with H.

Fig. 4 represents measurements at 2°.0. Here we are under both the transition points of lead-thallium, and of thallium. The magnetic field, though still below the initial field, is above the threshold field of thallium. Again the curve shows a linear increase of w with H.

The point for the field O does not lie on the same straight line. This may have the same reason as the discontinuity at the transition point of thallium in the w-T-curve without a magnetic field.

Fig. 5 gives the relation between w and H at a temperature so little below the transition point of $Pb\,Tl_2$, that we could also reach the threshold values of the field for $Pb\,Tl_2$ and for lead. The region between the value of H for which the electrical resistance begins to come back and that for

which it has regained its normal value has been hatched. The threshold value of H for $Pb\,Tl_2$ has been indicated by a thin line, that for Pb by a

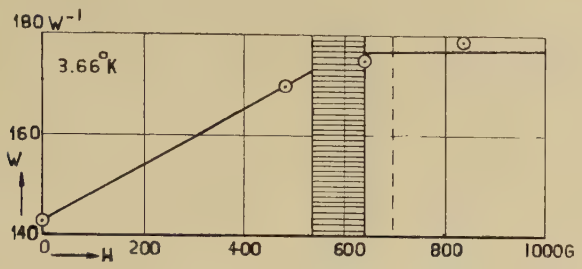

Fig. 5

dotted line. From the figure it is evident, that for high fields w does no longer increase linearly with H, but becomes practically constant when the

TABLE III
3.16°

H Gauss	W Watt^{-1}
0	133
481	174
642	190

TABLE IV
2.00°

H Gauss	W Watt^{-1}
0	131
214	140
481	168
749	192

TABLE V
3.66°

H Gauss	W Watt^{-1}
0	143
481	170
642	175
835	179

threshold field of $Pb\,Tl_2$ has been reached. The passage of the threshold value of Pb is of no consequence. The change observed here is of the order of the accuracy of the measurements.

In analogy with the figures 3 and 4 we have assumed a linear relation between w and H down to the initial field.

§ 3. Resuming we can say, that below the transition point of lead-thallium the thermal resistance increases linearly with magnetic fields under the threshold value of lead-thallium and remains practically constant, when that value has been reached. This result is interesting in two respects:

1°. According to the rule of LIPPMANN no magnetic field can penetrate into a supraconductor when starting from a field zero we stay below the threshold value; at a change of the field the intensity of the persisting currents along the surface only will be altered. We therefore might expect no influence of the external field on the thermal resistance. This expectation was proved right by our measurement with pure metals, as here we did not find such variations or at least very small ones.

2°. In magnetic fields above the threshold value the thermal resistance is greater than without a field, while for pure metals just the opposite influence of the field was found.

The latter phenomenon cannot be ascribed to the eventual occurrence of free thallium.

We must remark, that for tin we also found an increase of w in magnetic fields above the transition point; this change is however proportional with H^2 and much smaller.

In the case of lead-thallium the mentioned change is not observed above the transition point of lead-thallium; it must therefore be a property of the lead-thallium and not of the thallium.

To our opinion the phenomenon of the linear increase of w with H in fields below the threshold value of $Pb\,Tl_2$ must be interpreted as a gradual penetration of the field in the rod.

We might suppose the alloy to contain spots where the concentration of the lead atoms is very high and of others where the thallium atoms are dense. At the first places, where the field is lower than the threshold value of lead, it would hardly be possible for the field to penetrate. At the places with the great concentration of thallium atoms the field would be able to penetrate easily as long as we stayed above the transition point or above the threshold value of thallium.

Then we should have an intermediate case between the homogeneous supraconductive metal, for which the rule of LIPPMANN holds and into which the magnetic field cannot penetrate at all and the case of totally free electrons, the orbits of which the field can cross.

We intend to extend our investigations of these phenomena to other alloys.

Finally we express our thanks to Mr. J. DE NOBEL for his help during the measurements and with the calculations.

Mathematics. — *Ueber die Matrixgleichung* $XX' = A$. Von R. WEITZENBÖCK.

(Communicated at the meeting of April 2, 1932.)

Wir gehen aus von einer nicht-singulären symmetrischen Matrix $A = \| a_{ik} \|$ und fragen nach einer Matrix $X = \| x_{ik} \|$, die mit ihrer transponierten $X' = \| x_{ki} \|$ multipliziert, die Matrix A ergibt, die also die Gleichung

$$XX' = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

befriedigt. Hier ist A wegen $(XX')' = XX'$ notwendig symmetrisch. Wir geben im Folgenden zwei Wege an, die zur Lösung X von (1) führen.

Erste Methode. Wir bestimmen zuerst eine nicht-singuläre Matrix B mit

$$B^2 = A, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

was nach FROBENIUS [1]) rational ausführbar ist, wenn man die Eigenwerte von A kennt. B ist dann ebenfalls symmetrisch, d.h. $B' = B$ und wir haben:

$$XX' = A = B^2 = BB' \quad \text{oder} \quad B^{-1} XX' (B')^{-1} = E.$$

Setzen wir also

$$Y = B^{-1} X, \quad X = BY, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

dann wird

$$YY' = E, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

d.h. Y ist eine *orthogonale* Matrix und kann daher nach einem Satze von HERMITE [2]) in der Form

$$Y = (E - T) \cdot (E + T)^{-1}$$

dargestellt werden, wobei T eine beliebige alternierende Matrix mit $|E + T| \neq 0$ bedeutet. Wir erhalten also schliesslich nach (3):

$$X = \sqrt{A} \cdot (E - T)(E + T)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Zweite Methode. Wenn wir (1) in der Form $XEX' = A$ schreiben, können wir dies lesen: E ist kongruent mit A. Dann ist aber E auch allgemein äquivalent mit A, d.h. es gibt zwei nicht-singuläre Matrizes R und S mit

$$RES = A. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hier sind E und A symmetrisch; daher existiert nach FROBENIUS [3]) auch eine nicht-singuläre Matrix Z, die nur von R und S abhängt,

$$Z = S' \sqrt{R' S'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

und die E kongruent in A transformiert: $ZEZ' = A$. Nach (6) ist nun $R = AS^{-1}$, daher wird aus (7):

$$Z = S' \sqrt{(S')^{-1} AS^{-1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

wo S eine beliebige nicht-singuläre Matrix darstellt.

Ist nun X eine beliebige Lösung von (1), dann haben wir $XX' = ZZ' = A$; hieraus

$$Z^{-1} X \cdot X' (Z')^{-1} = E,$$

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[1]) G. FROBENIUS, Berliner Ber. (1896), p. 7—16; Vgl. auch diese Proceedings **35** (1932), p. 156—161.

[2]) CH. HERMITE, Crelle **47** (1853), p. 309; vgl. auch FROBENIUS, Crelle **84** (1878), p. 37.

[3]) Berliner Ber. l.c. oder auch P. MUTH, Theorie und Anwendung der Elementarteiler, Teubner (1899), p. 127.

oder für $Z^{-1}X = U$:

$$UU' = E,$$

d.h. U ist orthogonal. Also wird

$$X = ZU = S'\sqrt{(S')^{-1}AS^{-1}} \cdot (E-T)(E+T)^{-1} \quad . \quad . \quad . \quad (9)$$

mit beliebigem nicht-singulären S und alternierendem T mit $|E+T| \neq 0$ die allgemeine Lösung von (1). Aus (9) folgt $XX' = A$ und zwar auch bei singulärem A, d.h. (9) gilt auch für $|A| = 0$. Die Lösung (5) ist in (9) als Spezialfall enthalten, z.B. für $S = E$; aber auch allgemeiner, wenn wir in (9) $S = B^{-1}\sqrt{A}$ setzen, wo B eine nicht-singuläre symmetrische Matrix ist, wird $S'\sqrt{(S')^{-1}AS^{-1}} = \sqrt{A}$ und umgekehrt.

Hieraus ergibt sich schliesslich noch für $A = E$ eine irrationale Darstellung von orthogonalen Matrizen Y in der Gestalt

$$Y = S'\sqrt{(S')^{-1}S^{-1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

wo S eine beliebige nicht-singuläre Matrix bedeutet.

Mathematics. — *Über die Winkelableitung bei konformer Abbildung.* Von J. G. VAN DER CORPUT.

(Communicated at the meeting of April 2, 1932.)

Auf elementare und kurze Weise hat Herr C. VISSER [1]) bewiesen

Satz 1: *Es sei G ein Gebiet in der komplexen $w = u + iv$-Ebene, das alle Punkte enthält, die auf der positiven Achse rechts von einem geeignet gewähltem Punkt a liegen; für jedes $u \geq a$ möge $\chi(u)$ die obere Schranke von*

$$\frac{1}{u}\left(\left|\frac{u+W}{u-W}\right| - 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

bezeichnen, wo W den Rand von G durchläuft. Konvergiert das Integral

$$\int_a^\infty \chi(u)\,du, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

dann ist für jede in G reguläre analytische Funktion $z(w)$, die überall in G einen positiven Realteil bezitzt, der Quotient $\frac{z(u)}{u}$ beschränkt für alle Punkte u auf der positiven Achse rechts von a.

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[1]) C. VISSER, Sur la dérivée angulaire, Comptes Rendus de Paris **193** (1931), p. 1388.

Dieser Satz, der eine Rolle spielt in der Theorie[1]) der Winkelableitung bei konformer Abbildung, ist äquivalent mit

Satz 2: *Es sei die Funktion* $\omega(t) \geqq 0$ *für* $t \geqq 0$ *so definiert, dass das Integral*[2])

$$\int_1^\infty \left(\underset{0 \leqq q \leqq u}{Max}\ \omega(q)\right) \frac{du}{u^2} \quad \ldots\ldots\ldots \quad (3)$$

konvergiert. Für jede Funktion $z(w) = z(u + iv)$, *die im Gebiet*

$$G \ldots\ u > \omega(|v|), \qquad v \text{ beliebig},$$

regulär und analytisch ist, und einen positiven Realteil besitzt, ist der Quotient $\frac{z(u)}{u}$ *für alle auf der positiven Achse rechts von* $\omega(0) + 1$ *liegenden Punkte* u *beschränkt.*

Bemerkung: Die zur Zeit schärfsten Ergebnisse in der Theorie der Winkelableitung danken wir Herrn AHLFORS (1930). Zwar kann man Satz 2 aus seinen Resultaten ableiten, aber der hier mittels des VISSERschen Satzes gegebene Beweis ist einfacher. Ein von Herrn WOLFF in 1930 gefundenes Resultat hat eine grosse Ähnlichkeit mit Satz 2, setzt aber etwas mehr voraus.

Um die Äquivalenz der Sätze 1 und 2 zu beweisen, bemerke ich, dass für jeden Punkt $W = U + iV$ und für jedes nicht mit W zusammenfallende positive u

$$\left.\begin{aligned} \frac{1}{u}\left(\left|\frac{u+W}{u-W}\right| - 1\right) &= \frac{1}{u}\left(\frac{\sqrt{(u+U)^2+V^2}}{\sqrt{(u-U)^2+V^2}} - 1\right) \\ &= \frac{4U}{\sqrt{(u-U)^2+V^2}\left(\sqrt{(u-U)^2+V^2}+\sqrt{(u+U)^2+V^2}\right)} \end{aligned}\right\} \quad (4)$$

ist.

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[1]) Für diese Theorie vergleiche man:

J. WOLFF, Sur une généralisation d'un théorème de SCHWARTZ, Comptes Rendus de Paris **183** (1926), S. 500—502.

C. CARATHEODORY, Ueber die Winkelderivierten von beschränkten, analytischen Funktionen, Sitzungsber. der Preuss. Akad. d. Wissenschaften, Physikalisch-Mathematische Klasse (1929), S. 39—54.

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[2]) Mit $\underset{0 < q < u}{Max}\ \omega(q)$ wird die obere Schranke von $\omega(q)$ im Intervall $0 \leq q \leq u$ gemeint.

Ich werde zunächst zeigen, dass Satz 2 aus Satz 1 folgt. Ich nehme an, dass die Voraussetzungen von Satz 2 erfüllt sind. Ich setze

$$\Omega(u) = \underset{0 \leqq q \leqq u}{Max}\ \omega(q),$$

sodass $\Omega(u)$ eine monotone nicht-abnehmende Funktion $\geqq \omega(u)$ ist, und das Integral

$$\int_1^\infty \frac{\Omega(u)}{u^2}\, du \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

konvergiert.

Ist $u > 0$, dann ist also

$$\frac{\Omega(u)}{u} = \Omega(u) \int_u^\infty \frac{dt}{t^2} \leqq \int_u^\infty \frac{\Omega(t)}{t^2}\, dt \to 0$$

für $u \to \infty$, sodass für hinreichend grosses u

$$\Omega(u) \leqq \tfrac{1}{2} u. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

ist.

Für jeden Randpunkt $U + iV$ von G ist

$$U = \omega(|V|);$$

bei hinreichend grossem u ist wegen (6) für jeden Randpunkt $U + iV$ von G mit $|V| \leqq u$

$$U = \omega(|V|) \leqq \Omega(u) \leqq \tfrac{1}{2} u.$$

Aus (4) folgt also für alle Randpunkte $W = U + iV$ von G

$$\underset{|V| \geqq u}{Max} \frac{1}{u}\left(\left|\frac{u+W}{u-W}\right| - 1\right) \leqq \underset{|V| \geqq u}{Max} \frac{4\,\omega(|V|)}{2\,V^2}$$

und ausserdem für hinreichend grosses u

$$\underset{|V| \geqq u}{Max} \frac{1}{u}\left(\left|\frac{u+W}{u-W}\right| - 1\right) \leqq \underset{|V| \geqq u}{Max} \frac{4\,\omega(|V|)}{\sqrt{(u - \frac{1}{2}u)^2}\cdot\sqrt{u^2}} = \frac{8\,\Omega(u)}{u^2},$$

sodass die in Satz 1 definierte Funktion $\chi(u)$ für hinreichend grosses u der Ungleichung

$$\chi(u) \leqq 2 \underset{q \geqq u}{Max} \frac{\omega(q)}{q^2} + 8\,\frac{\Omega(u)}{u^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

genügt.

Für $q \geqq t \geqq 1$ ist

$$\frac{\omega(q)}{q^2} \leqq \frac{\Omega(q)}{q^2} = 2\,\Omega(q) \int_q^\infty \frac{du}{u^3} \leqq 2 \int_q^\infty \frac{\Omega(u)}{u^3}\,du \leqq 2 \int_t^\infty \frac{\Omega(u)}{u^3}\,du,$$

also

$$\underset{q \geqq t}{Max}\ \frac{\omega(q)}{q^2} \leqq 2 \int_t^\infty \frac{\Omega(u)}{u^3}\,du,$$

somit

$$\left.\begin{aligned} \int_1^\infty \left(\underset{q \geqq t}{Max}\ \frac{\omega(q)}{q^2} \right) dt &\leqq 2 \int_1^\infty dt \int_t^\infty \frac{\Omega(u)}{u^3}\,du \\ &= 2 \int_1^\infty \frac{\Omega(u)}{u^3}\,du \int_1^u dt \leqq 2 \int_1^\infty \frac{\Omega(u)}{u^2}\,du \end{aligned}\right\}. \quad (8)$$

Wegen der Konvergenz des in (5) vorkommenden Integrales folgt aus (7) und (8), dass auch das in (2) auftretende Integral konvergiert, sodass die Behauptung von Satz 1, also auch die Behauptung von Satz 2 gilt.

Ich werde jetzt zeigen, dass auch umgekehrt Satz 1 aus Satz 2 folgt. Es seien die Voraussetzungen von Satz 1 erfüllt. Bezeichnet $G^\star$ den in der rechten Halbebene $u > 0$ liegenden Teil des Gebietes G, und ist $\chi^\star(u)$ die obere Schranke des in (1) genannten Ausdrucks, wenn W den Rand von $G^\star$ durchläuft, dann konvergiert das Integral

$$\int_a^\infty \chi^\star(u)\,du \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Denn liegt der Rand von G ganz in der linken Halbebene $u < 0$, dann ist die imaginäre Achse der Rand von $G^\star$, sodass dann der in (1) vorkommende Ausdruck, somit auch $\chi^\star(u)$ identisch verschwindet, und sonst ist $\chi^\star(u) = \chi(u)$, da der in (1) auftretende Ausdruck für $W = U + iV$ mit $U \geqq 0$ mindestens 0, für $W = U + iV$ mit $U < 0$ negativ, also kleiner ist.

Ich setze nun $\omega(t)$ gleich der unteren Schranke der Zahlen U, denen mindestens ein in $G^\star$ liegender Punkt $U + iV$ mit $|V| = t$ zugeordnet werden kann. Für jedes $t \geqq 0$ ist $\omega(t)$ definiert und $\geqq 0$, und existiert mindestens ein Randpunkt $\omega(t) \pm it$ von $G^\star$. Wegen (4), mit

$U + iV = \omega(t) + it$ angewendet, ist dann für jedes $t \geqq 0$ und jedes positive in G^* liegende u

$$\chi^*(u) \geqq \frac{2\,\omega(t)}{\sqrt{u^2+t^2}\cdot\sqrt{(u+\omega(t))^2+t^2}}, \quad \ldots \quad (10)$$

also

$$\int_t^{2t} \chi^*(u)\,du \geqq \frac{2\omega(t)}{\sqrt{(2t)^2+t^2}\cdot\sqrt{(2t+\omega(t))^2+t^2}} \int_t^{2t} du = \frac{2}{\sqrt{5}} \frac{\omega(t)}{\sqrt{(2t+\omega(t))^2+t^2}}.$$

Das Integral linkerhand strebt, wegen der Konvergenz des in (9) vorkommenden Integrals, bei unbeschränkt wachsendem t nach Null. Folglich strebt auch die rechte Seite nach Null, woraus hervorgeht $\frac{\omega(t)}{t} \to 0$ für $t \to \infty$, sodass $\omega(t) \leqq t$ für hinreichend grosses t, also $\omega(t) \leqq u + t$ für hinreichend grosses u ist. Wegen (10) hat man nun für hinreichend grosses u

$$\chi^*(u) \geqq \underset{0 \leqq t \leqq u}{Max} \frac{2\omega(t)}{\sqrt{u^2+u^2}\cdot\sqrt{(u+u+u)^2+u^2}} = \frac{1}{\sqrt{5}} \frac{1}{u^2} \underset{0 \leqq t \leqq u}{Max}\ \omega(t).$$

Da das Integral in (9) konvergiert, konvergiert also auch das in (3) auftretende Integral, sodass die Voraussetzungen von Satz 2 erfüllt sind. also Satz 1 aus Satz 2 folgt.

Mathematics. — *Einige Ungleichungen bei bestimmten Integralen.* Von J. G. VAN DER CORPUT.

(Communicated at the meeting of April 2, 1932.)

Satz 1: *Ist im Intervall $a < u < b$ (a darf $-\infty$ und b darf $+\infty$ sein) die Funktion $f(u)$ monoton nicht-abnehmend und $\geqq 0$, und haben in diesem Intervall $g(u)$ und $k(u)$ integrierbare Derivierten mit*

$$g(u) \geqq 0, \quad g'(u) \geqq 0, \quad \lim_{u \to b} k(u) = 0, \quad k'(u) \leqq 0, \quad \ldots \quad (1)$$

dann ist

$$\int_a^b f(u)\,g'(u)\,k(u)\,du \leqq -\int_a^b \left(\underset{u \leqq q < b}{Min}\ f(q)\,g(q)\right) k'(u)\,du,$$

falls das letzte Integral existiert.

Vorbemerkung: Mit $\underset{u \leqq q < b}{Min}\ f(q)\, g(q)$, bezw. $\underset{u \leqq q < b}{Max}\ f(q)\, g(q)$ wird die untere, bezw. obere Schranke von $f(q)\, g(q)$ im Intervall $u \leqq q < b$ gemeint.

Beweis: Im Intervall (a, b) ist für jedes Zahlenpaar q und u mit $q \geqq u$

$$f(q)\, g(q) \geqq f(q) \int_a^q g'(t)\, dt \geqq \int_a^q f(t)\, g'(t)\, dt \geqq \int_a^u f(t)\, g'(t)\, dt,$$

also

$$\underset{u \leqq q < b}{Min}\ f(q)\, g(q) \geqq \int_a^u f(t)\, g'(t)\, dt,$$

mithin

$$-\int_a^b \left(\underset{u \leqq q < b}{Min}\ f(q)\, g(q)\right) k'(u)\, du \geqq -\int_a^b k'(u)\, du \int_a^u f(t)\, g'(t)\, dt$$

$$= -\int_a^b f(t)\, g'(t)\, dt \int_t^b k'(u)\, du = \int_a^b f(t)\, g'(t)\, k(t)\, dt.$$

Satz 2: *Ist im Intervall $a < u < b$ (a darf $-\infty$ und b darf $+\infty$ sein) $f(u)$ monoton nicht-zunehmend und $\geqq 0$, und haben in diesem Intervall die Funktionen $g(u)$ und $k(u)$ integrierbare Derivierten mit*

$$\lim_{u \to a} g(u) = 0, \quad g'(u) \geqq 0, \quad k(u) \geqq 0, \quad k'(u) \leqq 0, \ldots \quad (2)$$

dann ist

$$-\int_a^b \left(\underset{a < q \leqq u}{Max}\ f(q)\, g(q)\right) k'(u)\, du \leqq \int_a^b f(u)\, g'(u)\, k(u)\, du,$$

falls das letzte Intergral existiert.

Beweis: Man ersetze im Beweis von Satz 1 das Zeichen $\geqq$ durch $\leqq$, auszer dem ersten Zeichen $\geqq$, das durch das Gleichheitszeichen zu ersetzen ist; überdies ersetze man das letzte Gleichheitszeichen in Beweis von Satz 1 durch $\leqq$, und schliesslich noch

$$\underset{u \leqq q < b}{Min} \quad \text{durch} \quad \underset{a < q \leqq u}{Max}.$$

Satz 3: *Ist im Intervall $a<u<b$ (a darf $-\infty$ und b darf $+\infty$ sein) $f(u)$ monoton nicht-zunehmend und $\geqq 0$, und haben in diesem Intervall $g(u)$ und $k(u)$ integrierbare Derivierten mit*

$$g(u)\geqq 0,\quad g'(u)\leqq 0,\quad \lim_{u\to a} k(u)=0,\quad k'(u)\geqq 0, \quad . \quad . \quad . \quad (3)$$

dann ist

$$-\int_a^b f(u)\,g'(u)\,k(u)\,du \leqq \int_a^b \left(\operatorname{Min}_{a<q\leqq u} f(q)\,g(q)\right) k'(u)\,du,$$

falls das letzte Integral existiert.

Beweis: Wird

$$u=a+b-U,\quad q=a+b-Q,\quad f(u)=F(U),\quad g(u)=G(U),\quad k(u)=K(U) \quad (4)$$

gesetzt, dann ist nach Satz 1

$$-\int_a^b f(u)\,g'(u)\,k(u)\,du=\int_a^b F(U)\,G'(U)\,K(U)\,dU$$

$$-\int_a^b \left(\operatorname{Min}_{U\leqq Q<b} F(Q)\,G(Q)\right) K'(U)\,dU=\int_a^b \left(\operatorname{Min}_{a<q\leqq u} f(q)\,g(q)\right) k'(u)\,du.$$

Satz 4: *Ist im Intervall $a<u<b$ (a darf $-\infty$ und b darf $+\infty$ sein) $f(u)$ monoton nicht-abnehmend und $\geqq 0$, und haben in diesem Intervall $g(u)$ und $k(u)$ integrierbare Derivierten mit*

$$\lim_{u\to b} g(u)=0,\qquad g'(u)\leqq 0,\qquad k(u)\geqq 0,\qquad k'(u)\geqq 0, \quad . \quad . \quad (5)$$

dann ist

$$\int_a^b \left(\operatorname{Max}_{u\leqq q<b} f(q)\,g(q)\right) k'(u)\,du \leqq -\int_a^b f(u)\,g'(u)\,k(u)\,du,$$

falls das letzte Integral existiert.

Beweis: Werden U, Q, F, G und K durch (4) definiert, dann ist nach Satz 2

$$\int_a^b \left(\operatorname{Max}_{u\leqq q<b} f(q)\,g(q)\right) k'(u)\,du=-\int_a^b \left(\operatorname{Max}_{a<Q\leqq U} F(Q)\,G(Q)\right) K'(U)\,dU$$

$$\leqq \int_a^b F(U)\,G'(U)\,K(U)\,dU=-\int_a^b f(u)\,g'(u)\,k(u)\,du.$$

Satz 5: *Es sei im Intervall $a<u<b$ (a darf $-\infty$ und b darf $+\infty$ sein) $F(u)\geqq 0$, und es mögen in diesem Intervall $g(u)$ und $k(u)$ integrierbare Derivierten besitzen.*

Gilt stets (1), dann ist

$$\int_a^b \left(\operatorname*{Min}_{u\leqq q<b} F(q)\right) g'(u)\,k(u)\,du \leqq -\int_a^b \left(\operatorname*{Min}_{u\leqq q<b} F(q)\,g(q)\right) k'(u)\,du\,; \quad (6)$$

gilt stets (2), dann ist

$$-\int_a^b \left(\operatorname*{Max}_{a<q\leqq u} F(q)\,g(q)\right) k'(u)\,du \leqq \int_a^b \left(\operatorname*{Max}_{u\leqq q<b} F(q)\right) g'(u)\,k(u)\,du\,; \quad (7)$$

gilt stets (3), dann ist

$$-\int_a^b \left(\operatorname*{Min}_{a<q\leqq u} F(q)\right) g'(u)\,k(u)\,du \leqq \int_a^b \left(\operatorname*{Min}_{a<q\leqq u} F(q)\,g(q)\right) k'(u)\,du, \quad (8)$$

und gilt stets (5), dann ist

$$\int_a^b \left(\operatorname*{Max}_{u\leqq q<b} F(q)\,g(q)\right) k'(u)\,du \leqq -\int_a^b \left(\operatorname*{Max}_{a<q\leqq u} F(q)\right) g'(u)\,k(u)\,du, \quad (9)$$

jedesmal natürlich unter der Voraussetzung, dass das rechterhand auftretende Integral existiert.

Beweis: Man wende

Satz 1 mit $f(u)=\operatorname*{Min}_{u\leqq q<b} F(q)$; Satz 2 mit $f(u)=\operatorname*{Max}_{u\leqq q<b} F(q)$;

Satz 3 mit $f(u)=\operatorname*{Min}_{a<q\leqq u} F(q)$; Satz 4 mit $f(u)=\operatorname*{Max}_{a<q\leqq u} F(q)$

an.

Satz 6: *Es mögen die Funktionen $f(u)$, $g(u)$, $h(u)$ und $k(u)$ im Intervall $a<u<b$ (a darf $-\infty$ und b darf $+\infty$ sein) so gewählt werden, dass $g(u)$, $h(u)$ und $k(u)$ integrierbare Ableitungen besitzen, und*

$$f(u)\geqq 0,\ \lim_{u\to a} g(u)=0,\ g'(u)\geqq 0,\ \lim_{u\to b} h(u)=0,\ h'(u)\leqq 0,\ k(u)\geqq 0$$

ist.

Behauptungen: 1. *Ist stets* $k'(u) \geqq 0$, *dann ist*

$$\int_a^b \underset{u \leqq q < b}{(Max} f(q)\, g(q)\, h(q))\, k'(u)\, du \leqq -\int_a^b \underset{u \leqq q < b}{(Max} f(q))\, g'(u)\, du \int_u^b h'(t)\, k(t)\, dt,$$

angenommen, dass das Integral rechterhand existiert.

2. *Ist stets* $k'(u) \leqq 0$, *dann ist*

$$-\int_a^b \underset{a < q \leqq u}{(Max} f(q)\, g(q)\, h(q))\, k'(u)\, du \leqq -\int_a^b \underset{a < q \leqq u}{(Max} f(q))\, h'(u)\, du \int_a^u g'(t)\, k(t)\, dt,$$

vorausgesetzt, dass das rechts auftretende Integral existiert.

Beweis: 1. Es sei stets $k'(u) \geqq 0$. Ersetzt man $g(u)$ durch $h(u)$, dann gilt (5), sodass nach (9), mit $F(u) = f(u)\, g(u)$ angewendet,

$$\left.\begin{aligned} &\int_a^b \underset{u \leqq q < b}{(Max} f(q)\, g(q)\, h(q))\, k'(u)\, du \leqq \\ &-\int_a^b \underset{a < q \leqq u}{(Max} f(q)\, g(q))\, h'(u)\, k(u)\, du \end{aligned}\right\} \quad \ldots \quad (10)$$

ist. Ersetzt man $k(u)$ durch

$$-\int_u^b h'(t)\, k(t)\, dt,$$

dann wird $k'(u)$ durch $h'(u)\, k(u)$ ersetzt, und dann gilt (2), sodass nach (7), mit $F(u) = f(u)$ angewendet,

$$\left.\begin{aligned} &-\int_a^b \underset{a < q \leqq u}{(Max} f(q)\, g(q))\, h'(u)\, k(u)\, du \leqq \\ &-\int_a^b \underset{u \leqq q < b}{(Max} f(q))\, g'(u)\, du \int_u^b h'(t)\, k(t)\, dt \end{aligned}\right\} \quad \ldots \quad (11)$$

ist. Aus (10) und (11) folgt die erste Behauptung von Satz 6.

2. Es sei stets $k'(u) \leqq 0$. Dann gilt (2), sodass nach (7), mit $F(u) = f(u)\ h(u)$ angewendet,

$$\left.\begin{aligned} -\int_a^b \underset{a<q\leqq u}{(Max}\ f(q)\ g(q)\ h(q))\ k'(u)\ du \leqq \\ \int_a^b \underset{u\leqq q<b}{(Max}\ f(q)\ h(q))\ g'(u)\ k(u)\ du \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

ist. Ersetzt man $g(u)$ durch $h(u)$, und $k(u)$ durch

$$\int_a^u g'(t)\ k(t)\ dt,$$

dann wird $k'(u)$ durch $g'(u)\ k(u)$ ersetzt, und dann gilt (5), sodass nach (9), mit $F(u) = f(u)$ angewendet,

$$\left.\begin{aligned} \int_a^b \underset{u\leqq q<b}{(Max}\ f(q)\ h(q))\ g'(u)\ k(u)\ du \leqq \\ -\int_a^b \underset{a<q\leqq u}{(Max}\ f(q))\ h'(u)\ du \int_a^u g'(t)\ k(t)\ dt \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (13)$$

ist. Aus (12) und (13) folgt die zweite Behauptung von Satz 6.

Satz 7: *Es seien c und β positiv; es sei $\omega(u) \geqq 0$ für $u > c$, und es bezeichne $k(u)$ für $u > c$ eine positive Funktion mit integrierbarer Ableitung.*

Behauptungen. 1. *Ist für $u > c$ stets $k'(u) \geqq 0$ und $u^3\,\omega(u)$ monoton nicht-abnehmend, dann ist*

$$\int_c^\infty \underset{q\leqq u}{(Max}\ \omega(q))\ k'(u)\ du \leqq \beta \int_c^\infty \frac{\omega(u)}{u} k(u)\ du, \quad . \quad . \quad . \quad (14)$$

falls das letzte Integral existiert.

2. *Ist für $u > c$ stets $k'(u) \geqq 0$ und $\frac{\omega(u)}{u^3}$ monoton nicht-zunehmend, und auszerdem $\frac{\omega(u)}{u^3}\ k'(u)$ im Intervall $c < u \leqq 2c$ integrierbar, dann ist*

$$\int_c^\infty (Max_{q \geqq u}\, \omega(q))\, k'(u)\, du \leqq$$

$$(\beta+1) \int_c^\infty \frac{\omega(u)}{u^3 k(u) \left(\int_u^\infty \frac{dt}{t^2 k(t)} \right)^2} du + c^\beta \int_c^\infty \frac{\omega(u)}{u^\beta} k'(u)\, du, \Bigg\} \quad (15)$$

falls das erste Integral rechterhand existiert (das Schlussintegral existiert dann auch).

3. *Ist für $u > c$ stets $k'(u) \leqq 0$ und $\frac{\omega(u)}{u^\beta}$ monoton nicht-zunehmend, dann ist*

$$-\int_c^\infty (Max_{c < q \leqq u}\, \omega(q))\, k'(u)\, du \leqq \beta \int_c^\infty \frac{\omega(u)}{u} k(u)\, du + \omega(c)\, k(c), \quad . \quad . \quad (16)$$

falls das Integral rechterhand existiert (mit $\omega(c)\, k(c)$ wird der Grenzwert $\lim_{u \to c} \omega(u)\, k(u)$ gemeint, der eldlich vorausgesetzt wird).

4. *Ist für $u > c$ stets $k'(u) \leqq 0$ und $u^\beta \omega(u)$ monoton nicht-abnehmend, dann ist*

$$-\int_c^\infty (Max_{c < q \leqq u}\, \omega(q))\, k'(u)\, du \leqq (\beta+1) \int_c^\infty \frac{u\, \omega(u)}{k(u) \left(\frac{c}{k(c)} + \int_c^u \frac{dt}{k(t)} \right)^2} du, \quad (17)$$

vorausgesetzt, dass das letzte Integral existiert.

Vorbemerkung: Jede dieser vier Behauptungen liefert insbesondere die Existenz des linkerhand auftretenden Integrales.

Beweis: 1. Aus Satz 4, mit

$$a = c, \quad b = \infty, \quad f(u) = u^\beta\, \omega(u) \quad \text{und} \quad g(u) = u^{-\beta}$$

angewendet, folgt (14).

2. Die erste Behauptung von Satz 6, mit

$$a = c, \quad b = \infty, \quad f(u) = \frac{\omega(u)}{u^\beta}, \quad g(u) = \frac{u^\beta - c^\beta}{\int_u^\infty \frac{dt}{t^2 k(t)}} \quad \text{und} \quad h(u) = \int_u^\infty \frac{dt}{t^2 k(t)}$$

angewendet, gibt

$$\left.\begin{aligned}\int_c^\infty \left(\underset{q \geqq u}{Max}\ \omega(q)\,\frac{q^\beta - c^\beta}{q^\beta}\right).k'(u)\,du &\leqq \int_c^\infty \frac{\omega(u)}{u^\beta}\,.\,g'(u)\,du \int_u^\infty \frac{dt}{t^2} \\ &= \int_c^\infty \frac{\omega(u)}{u^{\beta+1}}\,g'(u)\,du.\end{aligned}\right\}. \tag{18}$$

Wegen

$$\int_u^\infty \frac{dt}{t^2\,k(t)} \leqq \frac{1}{k(u)} \int_u^\infty \frac{dt}{t^2} = \frac{1}{u\,k(u)}$$

ist

$$g'(u) = \frac{\beta\,u^{\beta-1}}{\displaystyle\int_u^\infty \frac{dt}{t^2\,k(t)}} + \frac{u^\beta - c^\beta}{\left(\displaystyle\int_u^\infty \frac{dt}{t^2\,k(t)}\right)^2} \cdot \frac{1}{u^2\,k(u)}$$

$$< (\beta+1)\,\frac{u^{\beta-2}}{k(u)\left(\displaystyle\int_u^\infty \frac{dt}{t^2\,k(t)}\right)^2},$$

sodass aus (18) folgt

$$\int_c^\infty \left(\underset{q \geqq u}{Max}\ \omega(q)\,.\,\frac{q^\beta - c^\beta}{q^\beta}\right).k'(u)\,du \leqq (\beta+1) \int_c^\infty \frac{\omega(u)}{u^3 k(u)\left(\displaystyle\int_u^\infty \frac{dt}{t^2\,k(t)}\right)^2}\,du, \tag{19}$$

wo das letzte Integral nach der Voraussetzung existiert. Folglich ist

$$\left.\begin{aligned}\int_{2c}^\infty \left(\underset{q \geqq u}{Max}\ \omega(q)\right)k'(u)\,du &\leqq \frac{1}{2^\beta - 1} \int_{2c}^\infty \left(\underset{q \geqq u}{Max}\ \omega(q)\,\frac{q^\beta - c^\beta}{q^\beta}\right)k'(u)\,du \\ &\leqq \frac{\beta+1}{2^\beta - 1} \int_c^\infty \frac{\omega(u)}{u^3 k(u)\left(\displaystyle\int_u^\infty \frac{dt}{t^2\,k(t)}\right)^2}\,du,\end{aligned}\right\} \tag{20}$$

sodass aus der Existenz des letzten Integrales hervorgeht, dass auch das erste Integral in (20) existiert. Aus (19) folgt dann (15) wegen

$$\int_c^\infty \left(\underset{q \geqq u}{Max}\, \omega(q) \cdot \frac{c^\beta}{q^\beta} \right) \cdot k'(u)\, du = c^\beta \int_c^\infty \frac{\omega(u)}{u^\beta} k'(u)\, du.$$

3. Satz 2, mit

$$a = c, \quad b = \infty, \quad f(u) = \frac{\omega(u)}{u^\beta}, \quad g(u) = u^\beta - c^\beta$$

angewendet, gibt

$$-\int_c^\infty \left(\underset{c < q \leqq u}{Max}\, \omega(q) \cdot \frac{q^\beta - c^\beta}{q^\beta} \right) \cdot k'(u)\, du \leqq \beta \int_c^\infty \frac{\omega(u)}{u} k(u)\, du,$$

sodass die dritte Behauptung aus

$$-\int_c^\infty \left(\underset{c < q \leqq u}{Max}\, \frac{\omega(q)}{q^\beta} c^\beta \right) k'(u)\, du \leqq -\frac{\omega(c)}{c^\beta} \cdot c^\beta \int_c^\infty k'(u)\, du \leqq \omega(c)\, k(c)$$

folgt.

4. Ich unterscheide zwei verschiedene Fälle, je nachdem $k(c)$ endlich ist oder nicht. Ist $k(c)$ unendlich, dann wende ich die zweite Behauptung von Satz 6 mit

$$a = c, \; b = \infty, \; f(u) = u^\beta\, \omega(u), \; g(u) = \int_a^u \frac{dt}{k(t)} \text{ und } h(u) = \frac{u^{-\beta}}{\int_a^u \frac{dt}{k(t)}}$$

an, und ich setze dann $\delta = 0$. Ist $k(c)$ endlich, dann wähle ich irgend eine positive Zahl δ, setze im Interval $0 < u < c$ $\omega(u) = 0$, und definiere in diesem Intervall die Funktion $k(u)$ so, dass sie eine integrierbare Ableitung $\leqq 0$ besitzt, und

$$\int_0^c \frac{dt}{k(t)} \geqq \frac{1}{1+\delta} \cdot \frac{c}{k(c)} \quad \ldots\ldots\ldots \quad (21)$$

ist; ich wende dann die zweite Behauptung von Satz 6 mit

$$a = 0, \; b = \infty, \; f(u) = u^\beta\, \omega(u), \; g(u) = \int_0^u \frac{dt}{k(t)} \text{ und } h(u) = \frac{u^{-\beta}}{\int_0^u \frac{dt}{k(t)}}$$

an.

In beiden Fällen bekomme ich

$$\left.\begin{aligned} -\int_c^\infty \underset{c<q\leqq u}{(Max}\ \omega(q))\, k'(u)\, du &\leqq -\int_c^\infty u^\beta\, \omega(u)\, h'(u)\, du \int_0^u dt \\ &= -\int_c^\infty u^{\beta+1}\, \omega(u)\, h'(u)\, du \end{aligned}\right\} \quad (22)$$

Wegen

$$\int_a^u \frac{dt}{k(t)} \leqq \int_a^u \frac{dt}{k(u)} \leqq \frac{u}{k(u)}$$

(a ist 0 oder c, je nachdem $k(c)$ endlich oder unendlich ist), ist

$$-h'(u) = \frac{\beta\, u^{-\beta-1}}{\int_a^u \frac{dt}{k(t)}} + \frac{u^{-\beta}}{\left(\int_a^u \frac{dt}{k(t)}\right)^2} \cdot \frac{1}{k(u)} \leqq \frac{(\beta+1)\, u^{-\beta}}{k(u)\left(\int_a^u \frac{dt}{k(t)}\right)^2} \quad . \quad (23)$$

Ist $k(c)$ endlich, dann ist für jedes $u \geqq c$ wegen (21)

$$\int_a^u \frac{dt}{k(t)} = \int_0^c \frac{dt}{k(t)} + \int_c^u \frac{dt}{k(t)} \geqq \frac{1}{1+\delta}\left\{\frac{c}{k(c)} + \int_c^u \frac{dt}{k(t)}\right\}, \quad . \quad . \quad (24)$$

und ist $k(c)$ unendlich, dann gilt diese Beziehung mit dem Gleichheitszeichen. Aus (22), (23) und (24) folgt

$$-\int_c^\infty \underset{c<q\leqq u}{(Max}\ \omega(q))\, k'(u)\, du$$

$$\leqq (1+\delta)^2(\beta+1) \int_c^\infty \frac{u\, \omega(u)}{k(u)\left(\frac{c}{k(c)} + \int_c^u \frac{dt}{k(t)}\right)^2}\, du\,,$$

wo $\delta = 0$ oder beliebig positiv ist. Hiermit ist (17) bewiesen.

Satz 8: Es sei $c > 0$ und $\gamma > 0$, und es sei $\omega(u) \geqq 0$ für $u > c$.

Behauptungen: 1. *Ist es möglich eine positive Zahl β so zu wählen, dass $\frac{\omega(u)}{u^\beta}$ monoton nicht-zunehmend ist, dann ist*

$$\gamma \int_c^\infty \underset{q\geqq u}{(Max}\ \omega(q))\, u^{\gamma-1}\, du \leqq (\beta + 3\gamma + 2\sqrt{\gamma(\beta+\gamma)}) \int_c^\infty \omega(u)\, u^{\gamma-1}\, du\,, \quad (25)$$

falls das letzte Integral existiert, und

$$\gamma \int_c^\infty (\underset{c<q\leqq u}{Max}\ \omega(q))\, u^{-\gamma-1}\, du \leqq \beta \int_c^\infty \omega(u)\, u^{-\gamma-1}\, du + \omega(c)\, .\, c^{-\gamma}; \quad . \quad (26)$$

für (26) wird nicht nur die Existenz des rechterhand auftretenden Integrales, sondern auch die Existenz des endlichen Grenzwertes $\omega(c) = \lim_{u \to c} \omega(u)$ *vorausgesetzt.*

2. *Ist es möglich eine positive Zahl* β *so zu wählen, dass* $u^\beta\, \omega(u)$ *monoton nicht-abnimmt, dann ist*

$$\gamma \int_c^\infty (\underset{q\geqq u}{Max}\ \omega(q))\, u^{\gamma-1}\, du \leqq \beta \int_c^\infty \omega(u)\, u^{\gamma-1}\, du \quad . \quad . \quad . \quad (27)$$

angenommen, dass das letzte Integral existiert, und

$$\gamma \int_c^\infty (\underset{c<q\leqq u}{Max}\ \omega(q))\, u^{-\gamma-1}\, du \leqq (\beta+2\gamma+2\sqrt{\gamma(\beta+\gamma)}) \int_c^\infty \omega(u)\, u^{-\gamma-1}\, du, \quad (28)$$

falls das letzte Integral existiert.

Beweis: 1. Ich wähle eine Konstante $\eta > \beta + \gamma$. Die erste Behauptung von Satz 6, mit

$$a = c, \quad b = \infty, \quad f(u) = u^{-\beta}\, \omega(u), \quad g(u) = u^\eta - c^\eta, \quad h(u) = u^{\beta-\eta}$$

und $\quad k(u) = u^\gamma$

angewendet, gibt

$$\left.\begin{aligned} \gamma \int_c^\infty \left(\underset{q\geqq u}{Max}\ \omega(q) \frac{q^\eta - c^\eta}{q^\eta} \right) u^{\gamma-1}\, du \leqq \\ - \int_c^\infty u^{-\beta}\, \omega(u)\, .\, \eta u^{\eta-1}\, du \int_u^\infty (\beta-\eta)\, t^{\beta-\eta-1}\, .\, t^\gamma\, dt \\ = \frac{\eta(\eta-\beta)}{\eta-\beta-\gamma} \int_c^\infty \omega(u)\, u^{\gamma-1}\, du. \end{aligned}\right\} \quad (29)$$

Für $q \geqq u \geqq c$ ist

$$\frac{\omega(q)}{q^\eta} = \frac{\omega(q)}{q^\beta} \cdot \frac{1}{q^{\eta-\beta}} \leqq \frac{\omega(u)}{u^\beta} \cdot \frac{1}{q^{\eta-\beta}} \leqq \frac{\omega(u)}{c^\eta},$$

also

$$\gamma \int_c^\infty \left(\underset{q\geqq u}{Max}\ \frac{\omega(q)}{q^\eta} \, .\, c^\eta \right) u^{\gamma-1}\, du \leqq \gamma \int_c^\infty \omega(u)\, u^{\gamma-1}\, du,$$

sodass aus (29) folgt

$$\gamma \int_c^\infty (Max_{q \geqq u} \omega(q))\, u^{\gamma-1}\, du \leqq \left(\frac{\eta(\eta-\beta)}{\eta-\beta-\gamma} + \gamma\right) \int_c^\infty \omega(u)\, u^{\gamma-1}\, du,$$

gültig für jedes $\eta > \beta + \gamma$. Diese Formel verwandelt sich in (25), wenn

$$\eta = \beta + \gamma + \sqrt{\gamma(\beta+\gamma)}, \quad \text{also} \quad \frac{\eta(\eta-\beta)}{\eta-\beta-\gamma} + \gamma = \beta + 3\gamma + 2\sqrt{\gamma(\beta+\gamma)}$$

gewählt wird.

Aus Satz 2, mit

$$a = c, \quad b = \infty, \quad f(u) = u^{-\beta}\,\omega(u), \quad g(u) = u^\beta - c^\beta, \quad k(u) = u^{-\gamma}$$

angewendet, geht hervor

$$\gamma \int_c^\infty \left(Max_{c < q \leqq u} \omega(q) \frac{q^\beta - c^\beta}{q^\beta} \right) u^{-\gamma-1}\, du \leqq \int_c^\infty u^{-\beta}\,\omega(u) \,.\, \beta u^{\beta-1} \,.\, u^{-\gamma}\, du$$

$$= \beta \int_c^\infty \omega(u)\, u^{-\gamma-1}\, du,$$

woraus (26) wegen

$$\gamma \int_c^\infty \left(Max_{c < q \leqq u} \frac{\omega(q)}{q^\beta} c^\beta \right) u^{-\gamma-1}\, du = \gamma \frac{\omega(c)}{c^\beta} c^\beta \int_c^\infty u^{-\gamma-1}\, du = \frac{\omega(c)}{c^\gamma}$$

folgt.

2. Satz 4, mit

$$a = c, \quad b = \infty, \quad f(u) = u^\beta\,\omega(u), \quad g(u) = u^{-\beta}, \quad k(u) = u^\gamma$$

angewendet, gibt (27).

Um schliesslich (28) zu beweisen, wähle ich eine positive Zahl $\eta > \gamma$, und setze $\omega(u) = 0$ für $0 < u < c$. Nach der zweiten Behauptung von Satz 6, mit

$$a = 0, \quad b = \infty, \quad f(u) = u^\beta\,\omega(u), \quad g(u) = u^\eta, \quad h(u) = u^{-\beta-\eta} \text{ und } k(u) = u^{-\gamma}$$

angewendet, ist

$$\gamma \int_c^\infty (Max_{c < q \leqq u} \omega(q))\, u^{-\gamma-1}\, du \leqq$$

$$\int_c^\infty u^\beta\, \omega(u) \,.\, (\beta+\eta)\, u^{-\beta-\eta-1}\, du \int_0^u \eta\, t^{\eta-1}\, t^{-\gamma} \,.\, dt = \frac{\eta(\beta+\eta)}{\eta-\gamma} \int_c^\infty \omega(u)\, u^{-\gamma-1}\, du,$$

gültig für jedes $\eta > \gamma$. Hieraus folgt (28), wenn

$$\eta = \gamma + \sqrt{\gamma(\beta+\gamma)}, \quad \text{also} \quad \frac{\eta(\beta+\eta)}{\eta-\gamma} = \beta + 2\gamma + 2\sqrt{\gamma(\beta+\gamma)}$$

gewählt wird.

Verallgemeinerungen der in dieser Arbeit vorkommenden Resultate auf unendliche Reihen und auf mehrfache Integrale überlasse ich dem Leser. Ich nenne hier nur die Ergebnisse bei unendlichen Reihen, die der Vorbemerkung von Satz 7 entsprechen.

Satz 9: *Existiert eine positive Zahl β, derart dass $n^\beta \omega_n$ (n ganz $\geqq 1$) monoton nicht-abnehmend ist, sind ω_n, k_n und $k_{n+1} - k_n$ stets $\geqq 0$, und konvergiert*

$$\sum_{n=1}^{\infty} \frac{\omega_n k_n}{n}, \quad \textit{dann ist} \quad \sum_{n=1}^{\infty} (Max_{q \geqq n}\, \omega_q) \cdot (k_{n+1} - k_n)$$

gleichfalls konvergent.

Satz 10: *Existiert eine positive Zahl β, derart dass $\frac{\omega_n}{n^\beta}$ (n ganz $\geqq 1$) monoton nicht-zunehmend ist, ist stets $\omega_n \geqq 0$, $k_n > 0$ und $k_{n+1} - k_n \geqq 0$, und konvergiert*

$$\sum_{n=1}^{\infty} \frac{\omega_n}{n^3 k_n \left(\sum_{t=n}^{\infty} \frac{1}{t^2 k_t}\right)^2}, \quad \textit{dann ist} \quad \sum_{n=1}^{\infty} (Max_{q \geqq n}\, \omega_q)(k_{n+1} - k_n)$$

gleichfalls konvergent.

Satz 11: *Existiert eine positive Zahl β, derart dass $\frac{\omega_n}{n^\beta}$ (n ganz $\geqq 1$) monoton nicht-zunimmt, sind ω_n, k_n und $k_n - k_{n+1}$ stets $\geqq 0$, und konvergiert*

$$\sum_{n=1}^{\infty} \frac{\omega_n k_n}{n}, \quad \textit{dann ist} \quad \sum_{n=1}^{\infty} (Max_{1 \leqq q \leqq n}\, \omega_q)(k_n - k_{n+1})$$

gleichfalls konvergent.

Satz 12: *Existiert eine positive Zahl β, derart, dass $n^\beta \omega_n$ (n ganz $\geqq 1$) monoton nicht-abnimmt, ist stets $\omega_n \geqq 0$, $k_n > 0$ und $k_n - k_{n+1} \geqq 0$, und konvergiert*

$$\sum_{n=1}^{\infty} \frac{n\omega_n}{k_n \cdot \left(\sum_{t=1}^{n} \frac{1}{k_t}\right)^2}, \quad \textit{dann ist} \quad \sum_{n=1}^{\infty} (Max_{1 \leqq q \leqq n}\, \omega_q)(k_n - k_{n+1})$$

gleichfalls konvergent.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at High Temperatures. V. On the Cooling Correction of the Metal Calorimeter in Exact High Temperature Calorimetry.* By F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA.

(Communicated at the meeting of April 2, 1932.)

§ 1. The use of the metal calorimeter for exact high temperature calorimetry, as developed in recent years, involves the application of a correction for the leakage, occurring during the time necessary for the establishment of complete thermal equilibrium within the instrument. If the electro-motive force of the thermoelements indicating the increase of temperature of the metallic block above that of its environment is e_{τ_1} at the moment τ_1 and e_{τ_2} at the moment τ_2, the relation between those numbers, on assuming the validity of NEWTON's law of cooling, has the form:

$$^{N}ln\, e_{\tau_1} - {}^{N}ln\, e_{\tau_2} = k\,.\,(\tau_2 - \tau_1),$$

or, if ordinary logarithms are used:

$$^{10}log\, e_{\tau_1} - {}^{10}log\, e_{\tau_2} = 0{,}4343\,.\,k\,.\,(\tau_2 - \tau_1).$$

The factor k in this equation is called the "leakage modulus"; the knowledge of its exact value is of vital importance for the calculation of the temperature X, to which the metallic block would have been heated at the moment τ_0 of introduction of the heated object into the calorimeter, if its total amount of heat were given-off with an infinitely great velocity.

The value of k is found to be:

$$k = \frac{2{,}3026\,.\,(^{10}log\, e_{\tau_1} - {}^{10}log\, e_{\tau_2})}{(\tau_2 - \tau_1)}.$$

If e_τ is expressed in Mikrovolts and τ in minutes, k is expressed in Mikrovolts pro minute.

As for the extrapolation of e_τ to the moment τ_0, — the cooling correction to be applied is: $0{,}4343\,.\,k\,.\,(\tau_2 - \tau_0)$, — it is desirable to make this correction as small as possible; moreover, the extrapolation mentioned is the less uncertain, the more the interval of time $(\tau_2 - \tau_0)$, necessary for the establishment of complete heat-equilibrium within the instrument, is reduced.

From this it appears advantageous to diminish the value of k as much as possible by constructive means. However, by reducing k to an extraordinary small value, the minimum interval of time necessary for the establishment of thermal equilibrium may, on the other hand, be too much increased; so that one loses in accuracy on one side, what is gained on

the other. As the metal calorimeter does not allow an acceleration of the establishment of its heat-equilibrium by stirring, — as is the case in using a calorimeter-liquid, — a compromise must be found in such a way, that the product: $k.(\tau_2 - \tau_0)$ finally obtains the most desirable order of magnitude.

For this reason we have made a systematical study of the size and behaviour of the leakage-modulus k in its dependence on the special circumstances and on the particular construction of the apparatus.

§ 2. In the original calorimeter, used in our first measurements, the metallic block was suspended in a large DEWAR-flask, which, in its turn, was placed within a somewhat wider metallic cylinder in such a way, that a layer of air of about 1 cm. thickness remained between the outer wall of the DEWAR-vessel and the metallic cylinder, the latter being in direct contact with the water of the surrounding thermostat. The metallic block itself was on the exterior covered by a thin sheet of felt, so as to separate the inner wall of the DEWAR-vessel from the block and to protect the glass vessel from breaking. In this instrument the factor $k' = 0{,}4343 \,.\, k$ had a value of about: 0.0008. After removing the felt and replacing it by a metallic contact with the inner glass wall, consisting of piled-up strips of metal foil in the form of a flat, elastic layer, the curious fact was observed, that the new value of k' ($= 0.0005$) proved much to be *diminished* [1]). This remarkable fact, — which is rather contrary to the behaviour which could be expected, — was, independent of us, also observed by MAGNUS and HOLTZMANN [2]), who lowered the value of k' in this way from 0.0013 to 0.00065.

From this follows, that it is evidently possible arbitrarily to vary the leakage-modulus by the special construction of the apparatus. Momentaneously the contact between the inner glass wall and the metallic block is, in our much improved, recent construction of the calorimeter, obtained by filling up the space between the block and the inner glass wall with grained graphite. In the case of this new instrument the value of k' was reduced in this way to about a third part of its original value and lowered from 0.00061 to the extraordinarily small value of 0.00023. However, a closer examination taught us, that this value *did not remain constant,* but that the leakage-modulus regularly and slowly decreased with an increasing lapse of time, as may be seen from the following data: (see next page).

In this case a difference of temperature of 1° C. was equivalent to 2430 M.V., while the temperature of the surrounding water-jacket was kept constant at 19°,9865 C. From this it becomes evident that the leakage-modulus k of the instrument in this form is *not* a really constant, but a *variable* value, slowly decreasing with the increasing lapse of time. It must,

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[1]) Conf.: F. M. JAEGER and E. ROSENBOHM, these Proceed., **33**, (1930), 458.

[2]) A. MAGNUS and H. HOLTZMANN, Ann. d. Physik, (5), **3**, (1929), 591.

Difference of Temperature between the Calorimeter and the Water of the Thermostat (each time after 1 hour more):	Value of $k' = 0{,}4343 \, . \, k$	Difference of Temperature between the Calorimeter and the Water of the Thermostat (each time after 1 hour more):	Value of $k' = 0{,}4343 \, . \, k$
5354 M.V.		9181 M.V.	
	0.000238		0.000270
5180		8844	
	0.000236		0.000268
5014		8523	
	0.000233		0.000265
4855		8216	
	0.000233		0.000261
4701		7925	
	0.000232		0.000263
4408		7641	
	0.000233		0.000258
4268		7374	
	0.000230		0.000258
4134		6868	
	0.000228		
3883			
	0.000226		
3763			
	0.000225		
3648			
	0.000213		
2563			
	0.000206		
2491			

however, be remarked, that, on calculating the cooling correction, the influence of this variability of k is almost imperceptible: for k' is itself only a very small number and the time necessary for an experiment does never surpass $1\frac{1}{2}$ or 2 hours. Moreover, on observing the change of k' in its dependence on the time elapsed, the real change of k' can, at each moment, truly be taken into account. It then appears that the final correction to be applied, never influences the final value of $\bar{c}_p$ obtained, by more than about 0.1 %. So, for instance, we successively found the following values for the mean specific heats of *silver* (133.339 Gr.), on cooling from 397°.2 C. to 22°.1 C., when the calculations were made after 2, 3, 4 and 5 hours since the introduction of the object into the calorimeter:

after 2—3 hours: heat developed: 3657.7 cal.; $\bar{c}_p = 0.05870$.

after 2—4 hours: heat developed: 3656.2 cal.; $\bar{c}_p = 0.05868$.

after 2—5 hours: heat developed: 3655.5 cal.; $\bar{c}_p = 0.05866$.

From this example it becomes clear, that a prolongation of the experiments even to 5 hours, makes no more difference in the final result, than 0.07 % of the whole value. But the necessary extrapolation for determining the temperature of the metallic block at the moment τ_0, is no longer allowed in this way, as soon as the interval of time $(\tau_2 - \tau_0)$ becomes

rather considerable, or if the cooling object in the calorimeter undergoes a change of its condition, which is accompanied by a thermal effect protracted during a somewhat long interval of time, as was, for instance, observed in the case of *beryllium* heated at temperatures surpassing 500° C.

§ 3. The fact that k is not constant, at first view makes the impression as if NEWTON's law were no longer valid. However, there is no reason to doubt the soundness of the fundamental principle expressed by it: it is much more probable, that there are secondary causes present, influencing the way of cooling of the instrument in such a way, that only in appearance the law mentioned seems no longer to be obeyed. Immediately the suspicion arose, that the DEWAR-vessel might be the principal cause of these phenomena and experience has fully confirmed this supposition.

For this reason the inner metallic cylinder surrounding the vacuum-flask and separating it from the waterbath by a thin layer of air, was now perforated, so that the water was brought into immediate contact with the outer wall of the DEWAR-vessel.

If the DEWAR-vessel was completely removed and the metallic block thus immediately placed in the water, the modulus k was trebly increased; but at the same time it now proved to remain *practically constant*. After the DEWAR-vessel was once more replaced, but this time brought into immediate contact with the water, the whole problem at once proved to be solved: *for not only the value of k was now reduced to a suitable magnitude, but, moreover, it proved to become practically constant after a sufficiently short interval of time*, as may be seen from the following data:

Interval of time (in Minutes) after the introduction of the object into the calorimeter:	Value of k' ($= 0{,}4343 \cdot k$) in M.V. pro Min.:
30— 40	0.001289
35— 45	0.001254
40— 50	0.001220
50— 60	0.001224
60— 70	0.001234
70— 80	0.001218
70—130	0.001220
130—190	0.001223

It is clear, that after 40 or 50 minutes after the dropping of the heated body into the calorimeter had occurred, k' had become practically constant, having a magnitude, which is quite suitable to the purpose. Therefore, it

appears to be quite unnecessary, completely to reject the use of the DEWAR-vessel, as occasionally has been proposed by some authors [1]): its presence offers so many advantages, especially by allowing the regulation of the feasible value of k and the maintenance of the constant temperature in the apparatus, that the solution of the problem just mentioned, appears much more preferable.

The two conditions to be fulfilled in using the DEWAR-vessel within the calorimeter are, therefore, the following:

1. The space between the metallic block and the inner glass wall must be filled up with a well conducting material, such as grained graphite.
2. The outer wall of the DEWAR-vessel must be brought into immediate and persistent contact with the water in the thermostat-jacket.

§ 4. If these conditions are fulfilled, the correction: $0{,}4343 \,.\, k \,.\, (\tau_2 - \tau_0)$ proves to be most favourably reduced; its magnitude is then sufficiently small and the thermal equilibrium of the instrument ordinarily reached in so small an interval of time as 40 minutes after the introduction of the heated object into the calorimeter.

It must, however, finally be remarked, that notwithstanding this, a very slight variation of k in the first 60 minutes constantly manifests itself. This variation always presents itself in an analogous way and, therefore, cannot be wholly accidental, but must in some way still be connected with the reflection of the heat-radiation at the outer wall of the vacuum-vessel. We hoped also to eliminate this slight variation by removing the layer of water immediately adjacent to the outer glass wall, by the application of a stirrer within the inner part of the waterbath. But experience has taught us, that this is *not* the case: the way in which the constancy of k is reached is not appreciably changed by the action of this new stirrer, as can be deduced from the following numbers:

Time in Minutes elapsed since the introduction of the heated object:	Values of k' on stirring:
45— 55	0.001189
50— 60	0.001184
55— 65	0.001180
60— 70	0.001188
60—120	0.001182

By means of two calorimeters built according to these principles, but still differing in other details of secondary importance, comparative studies now are in progress in this laboratory with the purpose of checking the results,

[1]) Conf. e.g. W. A. ROTH, Zeits. f. Elektrochem., **35**, (1929), 298.

obtained with the same materials under different conditions and by independant observers. The experience hitherto gathered, has already proved the perfect reproducibility of the values obtained under similar conditions and the soundness of the method employed, yielding an exactness of the respective data of 0.1 or 0.2 %.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances between 0° and 1625° C. VI. On the Law of* NEUMANN-JOULE-KOPP-REGNAULT *concerning the Molecular Heat of Chemical Compounds in Function of the Atomic Heats.* By F. M. JAEGER and J. A. BOTTEMA.

(Communicated at the meeting of April 2, 1932.)

§ 1. By a series of experimental investigations of NEUMANN [1]) (1831), REGNAULT [2]) (1840), JOULE [3]) (1844), KOPP [4]) (1864), PAPE [5]) (1864) and others, it seemed finally to be proved, that the molecular heat-capacity of a chemical compound can be calculated from the atomic heats of its composing atoms in a simple "additive" way. This law is commonly expressed by saying, that the atoms preserve their individual, normal specific and atomic heats also in their combinations with each other. MEYER [6]) first proved that the law is only an approximate one, calculation and experiment agreeing the better, the more the molecular volume approaches the sum of the atomic volumes, a conclusion contested by VAN AUBEL [7]). In recent times occasionally doubt has arisen about the validity of the law. By comparison of the specific heats of the pure elements with those of their compounds, SCHIMPFF [8]) and SCHÜBEL [9]) tried to demonstrate, that deviations are present in the case of intermetallic compounds. SCHÜBEL, for instance, accepts the rule as an approximate one; he finds positive, as well as negative deviations, in most cases of no more than about 2 %, occasionally of 6 %, and *in*dependent of the temperature.

Recently TAMMANN and ROHMANN [10]) have again taken up the subject; they find, by comparison of the data in literature of the quantities of heat

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[1]) F. E. NEUMANN, Pogg. Ann. d. Phys., **23**, (1831), 32.

[2]) H. V. REGNAULT, Ann. de Chim. et Phys., (2). **73**, (1840), 5; (**3**), **1**, (1841), 129; (**3**), **9**, (1843), 322; Pogg. Ann. d. Phys., **51**, (1840), 44, 213; **53**, (1841), 60, 243; **62**, (1844), 50.

[3]) J. P. JOULE, Phil. Mag., (**3**), **25**, (1844), 334.

[4]) H. KOPP, Lieb. Ann. d. Chem., Suppl. **3**, (1864), 1; (1865), 290, 301.

[5]) C. PAPE, Pogg. Ann. d. Phys., **120**, (1863), 337, 579; **122**, (1864), 408; **123**, (1864), 277.

[6]) S. MEYER, Wien. Sitzb. **109**, (1901), 405; Drude's Ann. d. Phys., **2**, (1900), 135.

[7]) E. VAN AUBEL, Journ. de Phys., (**3**), **10**, (1901), 36.

[8]) H. SCHIMPFF, Zeits. f. phys. Chem., **71**, (1910), 257.

[9]) P. SCHÜBEL, Zeits. f. anorg. Chem., **87**, (1914), 81, 101, 109.

[10]) G. TAMMANN und A. ROHMANN, ibid, **190**, (1930), 227.

developed, for the free elements and a number of intermetallic compounds positive as well as negative discrepancies, independent of temperature, and evidently connected with the diminution or increase of the specific volume of the compound in comparison with the sum of the atomic volumes of the constituting elements.

However, since we were able to demonstrate, that even where no allotropism of the metals investigated occurs, reproducible values of $\bar{c}_p$ can, with metals, only be obtained, if they really are *stabilized* (see next paper), and that a great number of the data on $\bar{c}_p$ and c_p published in literature only correspond to *un*defined states of these metals, — it must be evident, that such a comparison has no significance as a decisive proof, as long as the data of c_p, and especially their variation with the temperature, are so uncertain as they are just now. Such a comparison is only possible, if the following conditions are fulfilled:

1°. The c_p-t-curves of the components and of the compounds must be determined by the same observers with the greatest possible accuracy and then the obtained numbers be compared for each temperature.

2°. Proof must be given that the numbers thus measured are perfectly reproducible and that they really correspond to the normal, stabilized condition of the objects investigated.

3°. The method used in determining the integral heat-quantities must be so reliable, that no errors surpassing a few tenths of a procent, even at the highest temperatures, can occur.

4°. Thorough tests by means of X-ray-analysis must insure the exclusive presence of either the pure components or of the real compound to be studied, without mixed crystals or admixtures of the free elements being any longer present. The method developed in this laboratory is now so improved and perfectioned, that the values of $\bar{c}_p$ obtained in favourable cases are certain within 0.1 or 0.2 %. In this way the determination of the specific heats in their dependence on the temperature, has become one of the most sensitive methods of discovering changes in the behaviour and in the internal condition of such metals. The problem about the validity of the law mentioned, therefore, was taken up by us some time ago; in this paper the first results obtained will be communicated.

§ 2. *Tin.* The mean specific heat of *tin* was determined by means of a lump of the purest [1]) *tin*, which was carefully melted and cast into the form of the usual vacuum crucibles, fitting exactly in the central opening of the calorimeter; then it was slowly cooled. The piece of *tin* thus obtained was suspended by means of a little hook made of silver; the lump of *tin* weighed 91.1967 Gr., the silver hook 0.5393 Gr. The thermoelement used was carefully calibrated at the boilingpoint of water under known pressure

[1]) Purest tin from E. MERCK; for the mean specific heat between 20° C. and 0° C. the value: **0.0538** has been used in the calculation of the small correction for Q_0.

(99°.964 C.), at the meltingpoint of tin (231°.84 C.) and at the meltingpoint of potassiumdichromate (397°.5 C.). With respect to the standard-couple compared with the nitrogengasthermometer-scale of DAY and SOSMAN, the deviations of this thermocouple were: at 100° C.: — 3.4 M.V.; at 150° C.: — 1.8 M.V.; at 190° C.: — 0.4 M.V.; at 220° C.: + 0.8 M.V.; at 231°.84 C.: + 1.1 M.V. These values proved to be in full accordance with the other corrections of the values of its thermoelectric force, as measured up to 1540° C.

The total amounts of heat delivered by 1 Gr. of *tin* between t^0 and 0° C. were found to be:

Temperature t in 0° C.:	Total Amount of Heat Q_0 developed between $t°$ and 0° C. in calor.:
100.215	5.5246
100.514	5.5492
100.584	5.5453
100.600	5.5672
151.00	8.4492
154.40	8.6282
190.166	10.7650
190.96	10.8061
218.60	12.5243
219.80	12.6380

As *tin* shows an allotropic change at 203° C., the last numbers correspond to the rhombic modification; indeed, they are about 10 % higher, than they would be calculated by extrapolation for the tetragonal modification. From the values: 100°.478 and 5.5466 cal.; 151° and 8.4492 cal., and 190°.563 and 10.7856 cal., the following formula for Q'_0 was calculated:

$$Q'_0 = 0.05393 \,.\, t + 0.111425 \,.\, 10^{-4} \,.\, t^2 + 0.15037 \,.\, 10^{-7} \,.\, t^3,$$

which equation is valid between 0° and 203° C., because, on cooling, the transformation-point at 13° C. is passed, without an allotropic change taking place.

From this c_p is calculated to be:

$$c_p = 0{,}05393 + 0{,}22285 \,.\, 10^{-4} \,.\, t + 0{,}45111 \,.\, 10^{-7} \,.\, t^2.$$

The true specific heat of the white, tetragonal (metastable) *tin* at 0° C., would, therefore, be: 0.05393. This number is in perfect agreement with BRÖNSTED's directly measured value[1]): 0.05382.

[1]) J. N. BRÖNSTED, Zeits. f. phys. Chem., **88**, (1914), 479. The true specific heat c_p of grey, cubic tin at the same temperature is smaller: **0.0496**, according to this author.

The atomic heat C_p of tetragonal *tin* between 0° or 13° and 203° C. can thus be calculated from the formula:

$$C_p = 6{,}4014 + 0{,}26454 \,.\, 10^{-2} \,.\, t + 0{,}53546 \,.\, 10^{-5} \,.\, t^2.$$

Temperature in 0° C.:	Atomic Heat C_p:
0	6.4014
20	6.4564
50	6.5470
100	6.7195
150	6.9187
190	7.0973
200	7.1447
232	7.3033 (extrap.)

IITAKA [1]) has determined the specific heat of *solid, rhombic* tin at 232° C. and that of *liquid* tin at the same temperature. The first value, represented by the point C in Fig. 1 proves to be somewhat greater than that indicated by the point *B*, which, for a temperature of 203° C., follows from the amount of heat delivered at that temperature, as calculated from the corresponding values at 218°.6 and at 219°.8 C. This means, that the atomic and specific heats of *α-tin* [2]) vary with the temperature in the way

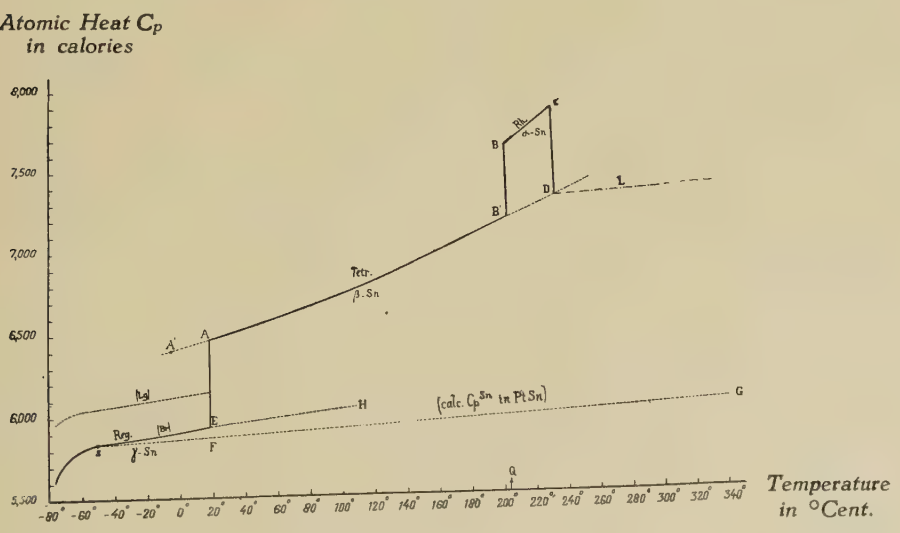

Fig. 1

[1]) I. IITAKA, Science Rep. Tohoku Univ., **8**, (1919), 99.

[2]) The transformation-temperature: tetragonal $\rightleftarrows$ rhombic tin lies at 202°.8 C., according to A. SMITS and H. L. VAN DER LEEUW, these Proceed., **15**, (1912), 681.

indicated in Fig. 1. His second value, — that for liquid tin, — is just the same, as the *extrapolated* value: 7.303 at 232° C., which follows from our own C_p-t-curve. Moreover, from PIONCHON's [1]) measurements of the specific heat of liquid tin between 250° and 1100° C., at least the temperature-coëfficient of c_p for liquid tin can approximately be deduced: it is very small, about 0.00105 for every 50°. If we start from the point D, the coëfficient corresponding to C_p approximately gives the direction of the curve L in Fig. 1. Finally, BRÖNSTED (loco cit.) has measured the true specific heats of grey tin: from these values the curve of the atomic heats of *γ-tin* is constructed. In this way the complete diagram, as represented in Fig. 1, can be deduced [2]).

§ 3. *The compound*: **PtSn.**

The specific heats of *platinum* and of *tin* now being exactly known, we have, — as a first example of a homopolar compound of two metals, — chosen the compound: *PtSn*. While *platinum* is cubic, *tin* either cubic, tetragonal or rhombic, the compound *PtSn* is hexagonal and its existence, therefore, easily controlable by means of *X*-ray analysis. While the *white* tin has tetragonal symmetry, with: $a_0 = 5.83$ Å., $c_0 = 3.16$ Å and $N = 4$, or, — which is equivalent to this, —: $a'_0 = 8.23$ Å., $c'_0 = 3.16$ Å., with $N' = 8$ and a diamond-like structure, which is compressed in the direction of the c-axis, — the *grey* tin is cubic, with $a_0 = 6.46$ Å. and $N = 4$. The smallest distance of two *Sn*-atoms in grey tin is: 2.80 Å., — a value which is quite comparable with that found in the case of *platinum*: 2.78 Å. Platinum is cubic, with a face-centred cell and $a_0 = 3.912$ Å.; $N = 4$ atoms pro cell. The compound *PtSn* (see Table I) is hexagonal, has the same type of structure as *NiAs*, and contains 2 molecules, i.e. the mass: Pt_2Sn_2 pro cell. Its density at 0° is: 13.1.

The compound *PtSn*, enclosed in a platinum vacuum crucible of the usual form (30.1341 Gr.) weighed 25.7467 Gr. Its chemical analysis yielded: 37.78 % *Sn* and 62.22 % *Pt*; the theoretical values are: 37.81 % *Sn* and 62.19 % *Pt*. An *X*-ray analysis by means of the powder-method gave the results collected in Table I.

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[1]) J. PIONCHON, Ann. de Chim. et Phys., (6), **11**, (1887), 33.

[2]) No more reliable values of c_p for grey tin than these are, as far as we know, available at this moment. The values determined by F. LANGE, Zeits. f. phys. Chem., **110**, (1924), 343, (dotted line *Lg* in Fig. 1) are somewhat higher than those of BRÖNSTED (loco cit.) and the number of both authors have been critizised by E. COHEN and A. L. TH. MOESVELD. Those of BRÖNSTED seem to be more reliable than LANGE's data. However, this does not make much difference for our purpose, as they are certainly *appreciably lower* than those for β-tin; our conclusion, that the values of C_p for tin in *PtSn* must be *nearer* to those of γ-, then to those of β- (and α-, or *liquid* tin), remains, therefore, in all cases quite justified. The transition-point: γ-tin $\rightleftarrows$ β-tin lies at 13° C.; conf. E. COHEN and Collab., Zeits. f. phys. Chem., **30**, (1899), 601; **33**, (1900), 57; **35**, (1900), 588; etc. Recent measurements yield 13° C. (COHEN).

TABLE I.

Powder-Spectogram of the Compound *Pt Sn* (tempered at 400° C.)
(*Crucible: 24*).

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:	$Sin^2\,\Theta$ (observed):	$Sin^2\,\Theta$ (calculated):	Indices (hkl):
1	45.4	1	β	11° 21′	0.0387	0.0383	(100)
2	50.4	4	α	12 36	0.0476	0.0469	(100)
3	54.3	1	β	13 34	0.0551	0.0548	(101)
4	60.2	4	α	15 3	0.0674	0.0670	(101)
5	75.4	3	β	18 51	0.1044	0.1040	(102)
6	79.4	3	„	19 51	0.1156	0.1149	(110)
7	83.8	10	α	20 57	0.1278	0.1272	(102)
8	88.4	8	„	22 6	0.1415	0.1407	(110)
9	97.2	1⁻ ?	β	24 18	0.1694	0.1694	(201) ?
10	102.9	1	α	25 43	0.1884	0.1875	(200)
11	108.9	1	„	27 14	0.2093	0.2076	(201)
12	111.9	2	β	27 58	0.2200	0.2184	(202)
13	114.0	1	α	28 30	0.2277	0.2278	(103)
14	124.9	4	„	31 14	0.2687	0.2679	(202)
15	138.1	1	„	34 31	0.3212	0.3216	(203) or (113)
16	140.2	1	„	35 3	0.3298	0.3281	(210)
17	141.3	1	β	35 20	0.3343	0.3342	(212)
18	144.6	1	α	36 9	0.3480	0.3482	(211)
19	149.6	1	„	37 24	0.3689	0.3684 or 0.3685	(203) or (204)
20	151.7	1	β	37 55	0.3777	0.3780	(114)
21	159.2	5	α	39 48	0.4100	0.4086	(212)
22	162.6	2	„	40 39	0.4243	0.4220	(300)
23	171.2	5	„	42 48	0.4616	0.4625	(114)
24	182.4	2	„	45 36	0.5105	0.5090 or 0.5091	(213) or (204)
25	191.5	1	„	47 52	0.5500	0.5494	(105)
26	198.7	5	„	48 41	0.5639	0.5625	(220)
27	205.5	1	„	51 22	0.6104	0.6090	(310)
28	210.1	1	„ (β)	52 32	0.6298	0.6291 or 0.6295	α (311) or β (106) and (401)
29	214.7	1	„	53 40	0.6498	0.6497	α_1 (214)

TABLE I. (*Continued*).

Powder-Spectogram of the Compound *Pt Sn* (tempered at *400°* C.)

(*Crucible: 24*).

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:	$Sin^2\,\Theta$ (observed):	$Sin^2\,\Theta$ (calculated):	Indices (hkl):
30	224.9	5	α	56° 14′	0.6893	0.6900	(205)
31	234.0	1	α (β)	58 15	0.7231	0.7232	α (006) or β (224)
32	238.3	5	α_1	59 34	0.7432	0.7434	α_1 (223)
33	239.1	1	α_2	59 47	0.7466	0.7436	α_2 (304) or β (321) and (206)
34	244.9	4	α_1	61 14	0.7682	0.7701	α_1 (106)
35	245.8	2	α_2	61 27	0.7716	0.7705	α_2 (401)
36	251.5	2	α (β)	62 52	0.7921	0.7982	α_2 (313) or β (322)
37	255.2	1	β	63 48	0.8050	0.8069	β (322)
38	263.0	5	α_1	65 45	0.8314	0.8304 or 0.8284	α_2 (402) or α_1 (215)
39	264.1	3	α_2	66 2	0.8348	0.8331	α_2 (215)
40	271.9	1	α_1	67 59	0.8584	0.8616	α_1 (116)
41	280.5	5	α_1	70 7	0.8845	0.8841	α_1 (224)
42	281.6	3	α_2	70 24	0.8876	0.8868	α_2 (224)
43	289.8	5	α_1	72 27	0.9091	0.9111	α_1 (321)
44	291.4	3	α_2	72 51	0.9131	0.9136	α_2 (206)
45	299.3	5	α_1	74 50	0.9315	0.9304	α_1 (403)
46	301.2	3	α_2	75 18	0.9356	0.9339	α_2 (314)
47	321.7	8	α_1	80 25	0.9723	0.9683	α_1 (322)
48	325.3	6	α_2	81 20	0.9772	0.9742	α_2 (322)

Radius of Camera: *57,2* m.M. Exposure: *70* m. Amp. hours.

Wave-length: $\lambda_\alpha = 1.540$ Å.; $\lambda_\beta = 1.388$ Å.; $\lambda_{\alpha_1} = 1.5374$ Å.; $\lambda_{\alpha_2} = 1.5412$ Å.

Quadratic Equation:

$$sin^2\,\Theta = 0.04696\,(h^2 + k^2 + hk) + 0.020125\,.\,l^2 \quad \ldots\ldots\ldots\

the hexagonal *compound* is present; it is identical with that studied in 1928 by OFTEDAHL [1]). No lines indicating either the presence of free platinum, or of free tin, were ever observed in the spectrograms.

§ 4. As the meltingpoint [2]) lies in the vicinity of 1281° to 1330° C., the mean specific heats can be determined over a considerable range of temperatures. At temperatures lower than 400° C., the accuracy of the determinations is, as a consequence of the predominant quantity of the platinum present, somewhat less than at higher temperatures; but the extreme precision of the experimental method gives us a guarantee, that also at 189° and 222° C. the data of $\bar{c}_p$ obtained possess a fair degree of accuracy. Indeed, the very flat curve, — almost a straight line, — joining the values of Q between 418° and 1045° C., equally passes through the other points in the graph representing Q_0 in function of t, even at the lower temperatures.

The small corrections of Q for the heat given off between the final temperature t' of the calorimeter and 0° C. were calculated by adopting the value 0.0398 for the mean specific heat of the substance within the interval from 20° to 0° C.; this certainly is very close to the truth.

Temperature t in ° C.:	Total Amount of Heat Q_0 between t and 0° C. in calor.:	Q'_0 as calculated from the formula:
189.74	7.3728	—
221.88	8.6419	8.6408
418.67	16.5282	16.5324
644 90	25.8917	—
718.30	28.9991	28.9982
802.06	32.5927	32.5867
1044.80	43.2606	—

These quantities of heat Q_0 can be expressed in function of t by the formula:

$$Q'_0 = 0{,}03836 \,.\, t + 0{,}25362 \,.\, 10^{-5} \,.\, t^2 + 0{,}0359597 \,.\, 10^{-8} \,.\, t^3,$$

and the specific heats of *PtSn*, therefore, by:

$$c_p = 0{,}03836 + 0{,}50724 \,.\, 10^{-5} \,.\, t + 0{,}107879 \,.\, 10^{-8} \,.\, t^2.$$

[1]) I. OFTEDAHL, Zeits. f. phys. Chem., **132**, (1928), 213.

[2]) F. DOERINCKEL, Zeits. f. anorg. Chem., **54**, (1907), 349; N. PODKOPAJEW, Journ. russ. phys.-chem. Ges., **40**, (1908), 249. Nach dem letztgenannten Autor liegt der Schmelzpunkt etwa bei 1330° C.

As the molecular weight of *PtSn* is 313.93, the molecular heat C'_p of the compound can be calculated from the equation:

$$C'_p = 12{,}0422 + 0{,}15924 \,.\, 10^{-2} \,.\, t + 0{,}33866 \,.\, 10^{-6} \,.\, t^2.$$

By means of this formula the values collected in Table II were obtained; simultaneously the values of C_p for pure *tin* and *platinum* at the same temperatures are, for the purpose of comparison, also given in Table II.

TABLE II.

Comparison of the Molecular Heat of *Pt Sn* and the Sum of the Atomic Heats of Platinum and Tin between 20° and 200° C.

Temperature in 0° C.	Atomic Heat of Tin (obs.):	Atomic Heat of Platinum (obs.):	Sum Σ:	Molecular Heat of *PtSn* (obs.):	Difference in calories:	Percentage defic. of Σ:
20	6.452	6.197	12.649	12.074	0.575	4.54 %
30	6.481	6.209	12.690	12.090	0.600	4.73
40	6.513	6.221	12.734	12.107	0.627	4.92
50	6.546	6.233	12.779	12.123	0.656	5.13
60	6.575	6.245	12.820	12.139	0.681	5.31
70	6.610	6.257	12.867	12.156	0.711	5.53
80	6.641	6.269	12.910	12.172	0.738	5.71
90	6.682	6.281	12.963	12.189	0.774	5.97
100	6.717	6.293	13.010	12.205	0.805	6.18
120	6.791	6.317	13.108	12.239	0.869	6.63
140	6.870	6.341	13.211	12.272	0.939	7.17
160	6.957	6.365	13.322	12.306	1.016	7.63
180	7.049	6.389	13.438	12.341	1.097	8.16
200	7.141	6.414	13.555	12.375	1.180	8.70

From these data it at once becomes clear, that the molecular heat of the compound *PtSn* is, at each temperature, *appreciably less than the sum of the atomic heats of the composing elements*, as observed at the same temperatures: the differences are 50 to 80 times as great, as the total experimental errors of the measurements.

There cannot be the least doubt, therefore, that the NEUMANN-JOULE-KOPP-REGNAULT-law is *not valid*: the differences range from 4.5 to 8.7 % of the additive values. Most remarkable is the fact, *that these differences are themselves a function of the temperature*; on a first approximation they increase linearly with the temperature.

The curve *FG* in Fig. 1 represents the values of C_p for *tin* in the compound, as calculated if it is supposed that the values of C_p for *platinum* in the compound are really preserved, — which certainly is *not* very probable, — as these, too, will be diminished to some extent.

The curve *FG* lies very close to the *extrapolated* curve *EH* for the *grey tin* (intersecting this curve at about —50° C.). If it is assumed, that the values of C_p for *platinum* in *PtSn* are equally different from those of the free element and are themselves also somewhat diminished (by about 0.05 to 0.10 calories), the curve *FG* would still be shifted a little upwards, in such a way, that it would practically coïncide with the (extrapolated) curve for grey tin in the metastable condition. It is obvious, that the calculated values of C_p for *tin* in the compound, do *not* manifest[1]) the discontinuities, characteristic of the allotropic transformations of pure tin; moreover, that these values doubtlessly very closely approach the extrapolated values for (metastable) grey tin. In this connection attention may also be drawn to the specific volumes of the compound and its components: as the specific weight of *PtSn* is 13.091 at 0° C. (2 mol. pro cell), that of *Pt* (4 atoms pro cell) 21.23 at the same temperature, and that of *grey tin*[2]) 5.751 at 18° C. (4 atoms pro cell), the rule of additive volumes would require:

$$2\left(\frac{195.23}{d_{Pt}}+\frac{118.7}{d_{Sn}}\right)=\frac{313.93}{d_{PtSn}},$$

or: $2\,(9.19+2.06)=24$. Actually the first member of this equation is: 23. This means, that the specific volume of the compound is a little greater (4 %) than the sum of the volumes of both components. If, in stead of the specific weight of *grey* tin, that of *white* (tetragonal) tin was used

[1]) If the values for pure *platinum* between 0° and 1275° C. are subtracted from the observed molecular heats of *PtSn*, as deduced from the experimental data, the following (virtual) values for C_p of *tin* in the compound are obtained:

Temp.	C_p (tin):	Temp.	C_p (tin):
0°	5.869	900°	6.458
100	5.912	1000	6.553
200	5.961	1100	6.652
300	6.014	1200	6.757
500	6.139	1275	6.840
700	6.287	1325	6.896

These (hypothetical) values of C_p for *tin* vary with the temperature in *a quite continuous* way.

[2]) E. COHEN and J. OLIE, Zeits. f. phys. Chem.. **71**, (1910), 400.

(=7.285), the agreement would be far less satisfactory: 21.64 instead of 24. From this consideration it may also be concluded, that the *tin* in *PtSn* is present in a condition, which is nearer to that of *grey*, than to that of white tin. Contrary to TAMMANN's and ROHMANN's suggestion (loco cit. p. 236), the heat-capacity of *PtSn* is *smaller* than the sum of those of the elements,although its specific volume is *greater* than the sum of the atomic volumes.

Further experiments of this kind now going on in this laboratory, will soon bring still stronger evidence of the fact, that the so-called "law of additive atomic heats" is certainly *not* valid for intermetallic, homopolar compounds. It is most probable then, that, *a fortiori*, it will be neither valid for *heteropolar* chemical compounds. Also this last conclusion will afterwards be tested by experiments.

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Geology. — *Migration and accumulation of oil and gas.* By J. VERSLUYS.

(Communicated at the meeting of April 2, 1932.)

Two points should be borne in mind when considering the occurrence of oil and gas in the earth's crust. Firstly, that they are encountered in the coarse sediments. Secondly, that the majority of the known oil and gas fields are situated in the highest parts of the structures, unless a fault acts as a barrier, in which case oil and gas accumulate in a coarse layer underneath it.

The problem of oil and gas concentration especially in the coarser strata was not at first considered by geologists, nor has it generally been recognized what filled the pores of the finer sediments. Without considering, properly, the reasons for the accumulation of oil and gas in the coarser sediments, the general opinion was that the coarser sediments are the only depositions which have sufficient pore space to contain oil, while the finer sediments were said to be tight. Accordingly the coarser beds, which have no exposures at the surface, are often erroneously regarded as closed reservoirs.

If it is taken for granted that oil and gas rise to the uppermost parts of the coarser strata owing to their lower specific gravity as compared to water[1]), and are retained there, a certain rôle is attributed to the finer grained strata, viz. that they act as barriers to the motion of oil and gas. As it has been remarked already, they were simply said to be tight. In the

[1]) With regard to buoyancy, the so called "shoreline pools" (XXI) and oil accumulations under planes of unconformity are under similar conditions as anticlinal fields.

argillaceous beds, however, there are fine pores and these are waterfilled. The reluctance of oil and gas to penetrate fine pored strata cannot be explained by frictional resistance of flow through such very fine pores, since the energy consumed by friction in liquids and gases when flowing through such strata approaches zero, as the motion becomes infinitely slow. This would mean that oil and gas could not be retained in a coarse bed for a geological period and hence all the oil and gas in the accumulations had not reached a stable state but would be still ascending.

In a former paper (XV) the writer argued that when accumulated oil or gas from a coarser porous medium penetrate a finer one, the pores of which are waterfilled, so that oil or gas would have to displace water which inversely would take the place the other fluids have made vacant, the total molecular energy must increase, so that then a certain amount of work is required to be done. In a similar way fine grained strata act as screens, when water, which has small globules of oil or bubbles of gas in suspension is forced through them (see XV). A certain pressure is needed to make an accumulated mass of oil or gas from a coarse bed penetrate a fine stratum and a force is needed to push fine globules of oil or bubbles of gas into a finer layer. Thus one can say that under the conditions prevailing in the earth's crust, viz. that all strata are water saturated, except where they are oil and gas bearing, the latter two are adverse to enter fine grained strata.

This aversion of oil and gas, when disseminated in water, may account for their accumulation at certain points in the earth's crust. Such accumulation would occur where a current of subterranean water from a coarser layer enters a fine layer and furthermore where such a current leaves a coarser portion of a layer to enter a finer portion of one and the same layer.

Instead of adhering to the old theory that buoyancy was the only cause of the tendency of oil and gas to accumulate in the highest parts of the structures, the writer in a former paper advanced the principle that the subterranean water which is squeezed out of the strata due to compaction, tends to rise at the anticlines. It flows longitudinally through the coarser strata towards the tops of the anticlines, here it ascends nearly vertically across both the coarser and the finer beds. So at the tops of the anticlines, on account of the aversion of oil and gas to enter a finer pored medium, they are retained in the coarser beds (XV).

Thus the compacting pressure squeezes oil and gas laden water out of the finer grained strata into the coarser beds. In the latter the water migrates longitudinally towards the crests, entraining the confined oil and gas. Near the crests however the upward transversal flow causes oil and gas to be screened out and remain in the coarser strata (XV). An investigation into the problem of subterranean water circulation, however, leads to the conclusion that not only does the water squeezed out by compaction flow longitudinally through the coarser beds towards the crests of the anticlines where it rises across all the strata (except at the anticlines in the

mountains or the foothills) but the same is true for the flow of water which could be called "the sub-continental circulation".

Part of the water precipitated from the atmosphere penetrates the earth's crust, percolates through the pores and drains mainly towards the nearby riverbeds. So does all the water percolating in the lowlands. A considerable portion of the water, however, which has penetrated the soil in the mountaneous regions and the highlands, follows a long path through the earth's crust and rises in the lowlands. It unites there with the percolation water of these regions and discharges into the river beds. Part of the percolation water from the continents drains towards the sea. It takes a long time, however, before the percolation water from the mountains or the highlands has displaced all the water which already filled the pores of the strata underlying the lowlands or the sea, so that the stage when percolation water which circulates through the coarser strata under the low lying regions and tends to rise there actually is percolation water, in many cases has not yet been reached. Thus, in many low lying regions, the ascending water is still more or less connate water which was confined in the strata at the time of their deposition. The percolation water of the high lying regions, which starts the *„sub-continental circulation"*, does not only enter the outcropping coarser layers but it also enters the outcropping finer layers. The coarse layers however are the real carrier beds, taking care of horizontal, or more properly, of the longitudinal transportation of the water — even when they have no exposures in the highlands or in the lowlands — whereas the water entering the exposed parts of the finer grained strata moves nearly perpendicularly across these layers until a coarser layer is reached.

In the highlands the motion through the finer grained strata generally has a downward trend whereas under the lower lying areas it rises vertically through the finer strata. Not only does the percolation water from the highlands — or the connate water which is pushed ahead of it — in this way ascend in the lowlands, but also does the excess water from compaction at depth as mentioned at the beginning of this paper rise in this way. On account of the pressure head of the water in the highlands and the mountains it often occurs that the water of each deeper coarse stratum tends to rise in a borehole to a higher level than that of the overlying beds, and this phenomenon in many low lying plains gives rise to the occurrence of artesian water (which has sufficient pressure head to rise above the surface of the earth). So one can say that the *potential* [1]) of the subterranean water under the lowlands as a rule tends to increase with depth (XIV). The difference of potential between two adjacent coarse beds may be considerable owing to the great resistivity of the parting finer bed. In one and the same coarse bed, however, the potential, although generally

[1]) This expression has been used by the writer since 1911. (Het beginsel der beweging van het grondwater, Amsterdam 1911). In 1914 it was also used in the report of the first Interstate Conference on artesian water in Australia.

decreasing from the mountains towards the middle of the plains, shows only slight variation over considerable distances. Therefore the potential in each one coarse layer in neighbouring anticlines and synclines is approximately the same. This means that in the anticlines the subterranean water with a certain potential lies nearer to the surface than in synclines, which makes the anticlines the most favourable places for the discharge of the underground water flow. Consequently most water of the sub-continental flow, which follows the coarser beds longitudinally, rises vertically at the anticline across both the finer and the coarser beds. (Probably the fact that water from a syncline following the trend of the layers comes nearer the surface in the adjacent anticline which is farther away from the mountains and the ascension of water across the beds at the anticlines, are responsible for the higher temperatures observed in many anticlines.) Where the water crosses a finer bed, the entrained globules of oil and bubbles of gas are withheld at the base of such a bed and they accumulate at the anticline. This principle — that anticlines are the places where water of underground circulation escapes — was evolved by the writer in 1930 (XV). J. L. RICH in a recent paper on other grounds comes to the conclusion that anticlines are the places where oil and gas from the water in the *„carrier beds"* [1]) accumulate. This geologist, however, lays more stress on an escape of water through fissures.

Probably the final concentration of oil and gas at the anticlines is aided by buoyancy (XV). When a certain amount of oil or gas has accumulated in the topmost portion of a coarse bed, buoyancy causes the oil or the gas to exert a certain pressure on the liquid in the overlying finer grained layer. At the crest of the structure the pressure is proportional to the height of the oil or gas accumulation, i. e. from the plane of contact of the edgewater and oil to the crest of the structure. It is counterbalanced by the intermolecular forces. These forces, however, can withstand but a certain pressure so that the height of the oil or gas accumulation cannot increase indefinitely. It is quite probable that in many cases the oil or the gas may penetrate the caprock and then they may partly or altogether rise to the next overlying coarse bed (see XV and XVII, p. 192). This perhaps explains why the plane of contact of oil or gas and edgewater in some coarse beds, separated by relatively thin shale layers may lie in the same level [2]).

It has already been mentioned, that along with the sub-continental flow of water which is stimulated by the percolation water of the highlands,

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1) The term "carrier beds" which was used by J. L. RICH expresses the idea very well.

2) The possibility that in some fields the oil is still rising to a higher horizon should not be precluded. The phenomenon that the higher horizons bear lighter oil than the deeper owing to adsorption, described by L. GURWITSCH ("The scientific principles of petroleum technology", London, 1926, pp. 127—128) when occurring is an indication that accumulated oil has ascended across argillaceous strata but it is also possible that this is still taking place.

also some water from the deeper strata, squeezed out by compacting pressure, has to discharge through the anticlinal folds.

In a former paper (XV) it has been set forth that not only are the argillaceous strata compressed, but that compaction also takes place in the coarser sandy strata. The compaction of the argillaceous strata is accomplished very easily and this is reversible. As it was emphasized formerly this compaction of the argillaceous strata is probably the main cause of the oil particles migrating into the coarser strata. It may or may not be finished before the structures are formed.

In the foregoing paragraph reference was made to the reversibility of compaction of argillaceous strata. The reversibility of compaction of clays is not complete, this has been proved by the laboratory experiments of C. TERZAGHI (XII) where clay after having been compressed, on expansion to its original pressure, did not entirely regain its original volume. C. TERZAGHI (XII) ascribed the compressibility of clay to elasticity of the particles, whereas the writer is of the opinion that for clay all phenomena of compression and expansion can be explained on the assumption that the water adsorbed at the surface bears a certain amount of potential energy, which increases when the mass is compressed and decreases when it expands (XIII). The inability of clay to expand to its original volume after compression, that is to say the incompleteness of the reversibility of compression, may be a consequence of a change of arrangement of the particles. The partial reversibility of the compaction of argillaceous strata is observed in boreholes; the shales expand when pressure is released and rise in the hole (the so called "heaving shales" see IV). The compaction of shales, however, has reached an equilibrium only under the prevailing compacting pressure. When water has an opportunity to escape from a shale it may be further compressed by the weight of the overlying strata. This phenomenon was the cause of the subsidence of the Goose Creek oil field (VII). So one can say that the argillaceous strata are in a state of equilibrium as long as the compacting pressure is not very large, and dissolution and recrystallisation have not commenced. Therefore, compaction of argillaceous strata may continue for a long time owing to a continued increase of burden and it is possible that after a period of rest, it will be resumed or reversed. Hence the migration of oil and gas from argillaceous beds into the coarser beds can be continuous, but it can also be interrupted and recommence afterwards.

The compaction of the arenaceous strata on the contrary is a more continuous phenomenon. The grains of sands can be crushed when pressure is sufficiently high but it has been proved experimentally (XIX) that the thickness of the superimposed strata, which could accomplish this, must be so great that before such crushing of the grains would take place, the arenaceous strata have been compacted probably, as described in a former paper, through dissolution and redeposition.

In a former paper (XV) the writer explained that the action of gravity

on the superimposed strata performs work, when the grains are dissolved at the points of contact, and at the same time material is deposited on the surface of the grains farther away from the point of contact, which means that compaction in this way will actually be established. This manner of compaction also applies to the argillaceous strata. E. RIECKE's conception (X) of this compaction was somewhat different.

The protracted compaction of the arenaceous and of the argillaceous strata may add some water to the sub-continental flow (XV) and in conjunction with this bring about the ascending motion of water at the anticlines, which in the writer's opinion is the main cause of accumulation of oil at the anticlines. The sub-continental flow however dominates. M. R. DALY (II) attributed the subterranean flow which in the present paper is denoted by "the sub-continental flow" to the "diastrophic" compaction which, however, in the writer's opinion is of less importance than the flow which is sustained by the percolation water of the high lying regions.

In the foregoing pages the theory is advanced, that accumulation of oil and gas at the anticlines has to be ascribed to compaction which forces these fluids from the argillaceous layers into the arenaceous beds.

The sub-continental circulation of subterranean water carries oil and gas through the crests of the anticlines, where the water rises vertically across the coarse and the fine beds both. Owing to the aversion of oil and gas to enter fine strata, they are left in the coarse strata near the crests. This would be the case if the texture of the arenaceous strata were homogeneous. When the texture however varies in one and the same bed, accumulation of oil and gas may occur in the coarser patches of such a bed.

In a former paper (XVI) the problem of the occurrence of oil and gas accumulation in the synclinal regions and on the flanks was treated. The theory that strata bearing oil or gas on the flanks and in the synclines should be dry or unsaturated was contradicted in that paper, and it was stated that such occurrence can quite well be attributed to differences in the texture of the strata. As stated previously, the aversion of oil and gas to penetrate a fine grained strata, tends to keep them in coarse patches of sandy strata. Thus when the sub-continental flow makes its way through a fine grained sand, oil and gas accumulate in the coarser patches. This explains why in most synclinal oil fields the edgewater encroachment as a rule is very slow. The oil occupies the coarser portions of the sand, while the finer grained parts are left to the edgewater. Therefore, in such fields oil may be propelled at a considerable rate towards the wells by the liberated gas, whereas a great resistance is offered to the flow of edgewater on account of the fineness of the pores outside the oil bearing part of the sand. This difference of texture may be accentuated through compaction, as the compaction through dissolution and redeposition stops as soon as the pores become oil or gas filled (see XV and XVII).

In many respects the writer's conception of accumulation agrees with the hydraulic theory of accumulation by M. J. MUNN (VI) and J. L. RICH

(IX). These authors, however, did not ascribe the anticlinal accumulation to the ascension of subterranean water at the anticlines, but they attributed it to an alteration of the velocity and the direction of the motion. Shortly after the writer published his first paper (XV) on the anticlinal discharge of subterranean water, J. L. RICH independently (XX) also brought forward a theory of the rise of water towards the anticline, but based on a different principle viz. that faults were responsible for it [1]).

There is another point which still further emphasizes the correctness of the above principles (see XVIII). D. HAGER (V) drew the attention to the inclination of the plane of contact between oil and water in anticlinal oil fields. He pointed out that the contact of oil and water in an anticlinal structure has a slope and that on the steeper side of the fold the water rises higher than on the flatter side and that oil extends further down the plunges than would be expected from observations on the flanks. HAGER did not refer to any literature, but his conception seems to be derived from C. H. BEAL's (I) description of the Cushing field in Oklahoma.

Very shortly before BEAL, J. L. RICH (VIII) described similar conditions for fields in Birds Quadrangle, Illinois. RICH gave an explanation of the phenomenon, which in the writer's opinion is the most probable and which quite agrees with the theoretical views set forth in the foregoing pages. RICH was of opinion that the inclination of the surface of contact is due to differences of pore sizes in the sand, or in other words, capillarity is an important factor in the shape of oil accumulations. The correctness of RICH's opinion is supported by the fact that the sand in which he observed an inclined plane of contact between oil and water, also contained smaller lenticular oil accumulations. C. H. BEAL in his above mentioned description of the Cushing field (I p. 39) remarks that the oil bearing sand was not of a uniform texture.

M. R. DALY (III) ascribed the deviation of the surface of contact between oil and gas in the Cushing field from a horizontal plane to the differentials of pressure which cause the motion of the water in the sand. These differentials in the opinion of said author are a consequence of diastrophic pressure. The writer believes that such differential pressures respectively differential potentials which in his opinion are caused mainly by differences of altitude at the surface may indeed have some bearing on the shape of the plane of contact, but it seems to him that the influence of capillarity is preponderent. The fact that in certain anticlinal oil fields the productive area is sagged, independent of the structure, may in the same way as the above described phenomena be attributed to differences of texture, if faults cannot account for it.

It often occurs in oil fields that a thin shale parting separates — at least

[1]) J. L. RICH's principle concerning the ascension of oil and water at the anticline are more fully explained in a new article (see: *Bull, Am Ass. Petr. Geol.*, March 1932, Vol. XVI, N°. 3, pag. 265) written by this author, which came to hand after the writer had finished his present paper.

over a limited area — an oil bearing top sand from a water bearing bottom sand. J. S. Ross (XI) recently described such a case but he mentioned that the bottom sand was calcarious and argillaceous. Perhaps in many such cases it is not exactly the thin parting layer which separates oil from water, but are the different conditions under and above this parting, caused by a difference of texture. Thin layers are liable to be broken, so that they could hardly establish a permanent partition.

It might be worth while to study all phenomena like irregularity of the boundaries of anticlinal oil fields, inclination of the plane of contact of oil and water from the standpoint, that variation of texture is an important factor in all matters of oil and gas accumulation. When such phenomena are encountered, they may indicate that the texture of the formation is irregular, so that accumulations are not of necessity limited to the anticline.

It may be concluded from the above pages:

1. that the most important factors in accumulation of oil and gas are:

a. the intermolecular forces which bring about an aversion of the disseminated as well as of the accumulated oil and gas to leave the coarser strata or the coarser portions of such,

b. the sub-continental groundwater circulation, which is the subterranean flow of water from the mountains and the highlands longitudinally through the coarser beds ascending in the lowlands mainly at the anticlines.

c. the discharge of the excess of water at depth created by compaction of strata: this discharge follows the same paths as the ascending water of the flow mentioned sub *b*,

d. compaction of argillaceous strata which forces the connate water they contain with disseminated oil and gas into the coarser beds;

2. that the rôle to be attributed to buoyancy is mainly to establish the final concentration of oil as well as gas during and after the accumulation by the continental groundwater circulation;

3. that the tardiness of edgewater encroachment during exploitation of certain fields which yield oil and gas quite readily, may be attributed partly to the differences of texture which are responsible for their accumulation, but also partly to the fact that compaction and cementation persist in the edgewater while they are discontinued where oil or gas fill the pores;

4. that synclinal oil and gas can only be expected in sands with tardy edgewater encroachment and an irregular shape of productive areas, where the irregularity is not caused by dislocations.

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Microbiology. — *On some physiological artefacts.* By A. J. KLUYVER and J. K. BAARS.

(Communicated at the meeting of April 2, 1932.)

§ 1. *Introduction.*

The existence and the wide distribution of thermophilic microbes, i.e. of micro-organisms which only proliferate at temperatures of 30° C. and higher, offer several problems to the physiologist. Mention may be made in this respect of the problem of active life at temperatures of 60—75° C.,

temperatures at which all known proteins are coagulated or denatured. No less astonishing is the fact that often by lowering the temperature of cultivation already at 30° C. multiplication is altogether prevented, which means that at this relatively high temperature a process occurs which can be compared to the "rigor frigoris" ("Kältestarre") of the mesophilic organisms. Finally there is the problem of the very general occurrence of thermophilic microbes in nature.

It is regarding this latter question that we will make here some remarks based chiefly on experiences gathered in a study of the bacteriology and biochemistry of natural sulphate reduction [1]).

It has been known since long that the distribution of thermophilic microbes is not at all restricted — as might be expected — to those spots on earth where high temperatures prevail. On the contrary already for many years experimental proof was furnished that practically all samples of soil and water examined contain germs of thermophilic microbes.

Several authors have drawn attention to this fact and have attempted to offer an explanation for this remarkable phenomenon.

So LYDIA RABINOWITSCH [2]) suggested that the thermophilic bacteria would multiply in the colon of warm-blooded animals and would only reach the actual finding-places together with the excrements of the animals.

This view, however, was severely critisized by LIESKE [3]), who pointed out that practically everywhere in soil species are encountered which do not show any growth at temperatures below 40° C. Moreover for some thermophilic *Actinomyces*-strains LIESKE brought the experimental proof that they did not multiply at all on passing the colon of rabbits, notwithstanding the fact that the mentioned micro-organisms could always be isolated from the excrements of the said animals.

Another explanation was forwarded by MIEHE [4]) who made a special study of the factors underlying the spontaneous heating of various vegetable materials. MIEHE has brought experimental proof that thermophilic micro-organisms are indispensable in the establishing of high temperatures during vegetable decay. So one cannot wonder that MIEHE, and partly also NOACK [5]), is inclined to explain the general occurrence of thermophilic organisms in nature by accepting a secundary distribution from these primary centers of multiplication.

Already LIESKE points out that this explanation is not very satisfactory either, with a view to the wide distribution in regions for which conditions favorable for the production of high temperatures by vegetable decay are very unlikely to occur.

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[1]) For details regarding this study the reader is referred to: J. K. BAARS, Over sulfaatreductie door bacteriën. Diss. Delft 1930.

[2]) L. RABINOWITSCH. Zeitschr. f. Hyg. **20**, 154, 1895.

[3]) R. LIESKE, Morphologie und Biologie der Strahlenpilze, Leipzig, 1921.

[4]) H. MIEHE, Die Selbsterhitzung des Heues. Jena, 1907; 2te Aufl. Berlin, 1930.

[5]) K. NOACK, Jahrb. f. wissensch. Botanik **51**, 593, 1912.

NOACK (l.c.) attributes great significance to the heating of the soil by solar radiation, especially in summer, as a factor in the multiplication of thermophilic micro-organisms. LIESKE is prepared to accept this explanation partly, but emphasizes that it cannot give a complete solution of the problem, since thermophilic germs are found in equal frequency in soils which are exposed to solar radiation as in soils for which a heating to the minimum temperature for the growth of thermophiles is certainly excluded (soils in thick forests, in shadowed rock clefts etc.).

LIESKE gives finally as his opinion that the greater part of the isolated thermophilic micro-organisms are nothing but forms of ordinary mesophilic microbes, which have underlied sudden changes in properties in consequence of the conditions prevailing during isolation.

However, LIESKE was unable to support this view experimentally: all pure cultures of *Actinomyces* species tested were unable to adapt themselves to pronounced changes in the temperature of cultivation.

So we may conclude that the problem of the wide distribution of thermophilic microbes in nature has remained unsolved until now. It seems to us that the observations reported below may throw some light on this question.

§ 2. *Observations on thermophilic sulphate reducing bacteria.*

It was BEIJERINCK [1]) who was the first to make a thorough investigation of the microbiological process of sulphate reduction and who gave a good description of the causal organism. This proved to be a strictly anaerobic bacterium the shape of which varied between that of a curved rod and that of a typical spirillum. In accordance with these findings the name of *Spirillum desulfuricans* — which was changed later into *Vibrio desulfuricans* — was proposed. His collaborator VAN DELDEN [2]) soon extended our knowledge of microbial sulphate reduction and succeeded in bringing *V. desulfuricans* into pure culture. Moreover VAN DELDEN isolated a closely related species *V. aestuarii* from mud of the North Sea coast and showed that this organism differed from *V. desulfuricans* by its ability to reduce sulphate in BEIJERINCK's medium only after the addition of 3 % sodium chloride.

Many years later ELION [3]) isolated a third species which was characterized by its ability to effect sulphate reduction at a temperature of 50—60° C. To this species, which was fully inactive at the optimal temperature of *V. desulfuricans* (30° C.) ELION gave the name of *V. thermodesulfuricans*.

It was a closer study of this latter species which led to some unexpected observations.

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[1]) M. W. BEIJERINCK, Centralbl. f. Bakt. 2te Abt. **1**, 49 und 104, 1895.
[2]) A. VAN DELDEN, Centralb. f. Bakt. 2te Abt. **11**, 81 und 113, 1904.
[3]) L. ELION, Centralbl. f. Bakt. 2te Abt. **63**, 58, 1924.

First of all it must be emphasized that *V. thermodesulfuricans* occupies a rather special place amongst the thermophilic bacteria described until now, owing to the fact that the great majority of these belong to the aerobic sporeforming bacilli. On the contrary *V. thermodesulfuricans* is a strictly anaerobic sporeless microbe of which no resting stages whatever are known. In accordance with this statement cultures of this bacterium are killed by the smallest traces of free oxygen as soon as the temperature is lowered to such a degree that active metabolism is prevented.

It is obvious that a bacterium with such properties is utterly unfit for a secundary distribution in nature and so one would expect that it could only be found in very restricted areas, where at some time temperatures higher than 30° C. would have reigned.

As a matter of fact experiences were quite incompatible with this deduction. ELION isolated the first strain of the new species from mud out of a ditch alongside the laboratory. Apart from the fact that the isolation was performed during the winter at a moment when the water in the ditch was covered with ice, it can be guaranteed that the temperature in the ditch and in the mud will reach under no conditions 30° C. Our first impression was therefore that we had to ascribe the said occurrence of *V. thermodesulfuricans* to an incidental cooperation of unknown factors.

However, it proved to be possible to find *V. thermodesulfuricans* quite regularly in all samples of mud tested and in many samples of soil as well.

The only way out of this impasse is to conclude that in nature no organism with the properties of *V. thermodesulfuricans*, i.o.w. an obligate thermophilic bacterium with sulphate reducing metabolism, exists. In this line of thought *V. thermodesulfuricans* should be nothing but an adaptate of the corresponding mesophilic organism to a higher temperature region. This means that we must consider *V. thermodesulfuricans* to be a physiological artefact produced under the conditions of the primary enrichment culture.

At first sight there seems to be a serious objection to accept this point of view. For if the pure culture of *V. desulfuricans* is tested on its ability to grow at a temperature of 55° C., no adaptation occurs and the result is quite negative.

However we were able to show that also in the pure culture remnants of the supposed adaptive power were still present on the understanding that adaptations to temperatures which are only slightly higher were still possible. Moreover it proved to be quite feasible to come to additional effects in this respect, i.e. to convert gradually a pure culture of *V. desulfuricans* into a pure culture of *V. thermodesulfuricans*.

The whole procedure is illustrated in Table I which will not want any further explanation, besides the statement that the figures given in the table represent mgr. H_2S produced in the course of the experiment, calculated pro Litre of the medium.

But also the reverse process could be realised, as is demonstrated in

TABLE I.

Conversion of *V. desulfuricans* into *V. thermodesulfuricans*.

Initial culture a, cultivated at 30° C.

Temperature of cultivation	30°	35°	40°	45°	50°	55°
Inoculated from *a*	b_1 : 510	b_2 : 510	b_3 : 420	b_4 : 40	b_5 : 20	b_6 : 17
„ „ b_3	—	—	—	c_1 : 301	c_2 : 36	c_3 : 18
„ „ c_1	—	—	—	—	d_1 : 326	d_2 : 112
„ „ d_2	—	—	—	—	—	e_1 : 415

Table II. In this Table the production of hydrogen sulphide (again calculated in mgr. pro Litre of culture medium) is given for successive

TABLE II.

Conversion of *V. thermodesulfuricans* into *V. desulfuricans*.

Designation of culture	Temperature of cultivation	Quantity of H_2S produced
Initial culture *a*	55° C.	480
b, inoculated from *a*	50° „	453
c, „ „ *b*	45° „	425
d, „ „ *c*	40° „	384
d', „ „ *d*	40° „	481
e, „ „ *d'*	35° „	143
e' „ „ *e*	35° „	322
e'', „ „ *e'*	35° „	350
f, „ „ *e''*	30° „	180
f', „ „ *f*	30° „	481
f'' „ „ *f'*	30° „	510

cultures at gradually lowered temperatures. It appears from this table that at various temperatures it was necessary to have a short series of reinoculations before optimal metabolic activity was attained.

Taking into consideration the ubiquity of *V. thermodesulfuricans* together with the practical impossibility of a secundary distribution of this organism in nature, these results seem to warrant the view that this species is nothing but an artefact produced under the conditions of the accumul-

ation experiment out of a pluripotent sulphate reducing bacterium occurring in nature.

It seems probable that the same holds good for most thermophilic organisms with ubiquitous occurrence in nature.

§ 3. *Observations on the adaptation of V. desulfuricans to media containing various concentrations of sodium chloride.*

Whilst the general applicability of the forwarded theory of thermophily remains to be proven by further experiments, we can refer here to some experimental evidence which tends to support the correctness of this view.

It could be demonstrated namely that the pronounced adaptive power of the naturally occurring sulphate reducing bacterium as contrasted with the more limited power of the pure culture was not restricted to adaptations to abnormal temperature regions. As a matter of fact we met with an exactly corresponding situation in a comparative study of *V. desulfuricans* and *V. aestuarii* van Delden.

As already mentioned *V. aestuarii* was isolated by VAN DELDEN from mud soaked with seawater and moreover was shown to be inactive in the usual nutrient medium to which no sodium chloride was added. Since at the other hand *V. desulfuricans* was fully inactive in this medium in case 3 % of sodium chloride was added, these facts apparently fully justify the distinction in species as carried through by VAN DELDEN.

We could easily confirm the correctness of the above statements of VAN DELDEN.

A pure culture of *V. desulfuricans* tested on its ability to grow in media with increasing concentrations of sodium chloride gave the following results:

Concentration NaCl in medium:	0	¾	1½	2¼	3 %
mgr. H_2S produced pro Litre:	397	325	200	87	40

Since the inoculation of the media involved the addition of a quantity of H_2S, corresponding to about 30 mgr. pro Litre, we learn from these figures that in the medium with 3 % NaCl practically no development of *V. desulfuricans* took place.

On the other hand a pure culture of a typical *V. aestuarii* gave the following results:

Concentration NaCl in medium:	0	1	2	3 %
mgr. H_2S produced pro Litre:	23	37	82	430

The pronounced divergency in behaviour of both species is sufficiently demonstrated by these figures.

Nevertheless we soon made the remarkable observation that it was quite feasible to isolate a strain with all the properties of *V. aestuarii* by starting from samples of mud which were practically devoid of sodium chloride.

It is obvious that this situation shows a great similarity to that which was reported in § 2 with regard to *V. thermodesulfuricans*. So we were led to the conclusion that the strains of *V. aestuarii* isolated from the salt free

mud again were artefacts produced under the conditions of the enrichment culture out of a pluripotent sulphate reducing bacterium.

But then it would be probable that also the pure cultures of both species would have preserved part of their adaptive power and therefore could be gradually converted into each other.

The experiments proved to be in agreement with this presumption. For the sake of brevity we will refrain from reproducing here the results, which can be found in the thesis of BAARS.

It seems of more importance to mention here another phenomenon which presented itself when various pure strains of *V. desulfuricans* were tested on their ability to grow in salt containing media. It was found that this ability was markedly dependent on the time during which the strain had been previously cultivated in the laboratory, notwithstanding all pure cultures were regularly reinoculated into fresh media about every four of five weeks.

This is demonstrated in Table III, in which the figures represent again mgr. of H_2S produced pro Litre of culture medium.

TABLE III.

Relation between the age of culture of various strains of *V. desulfuricans* and their ability to grow in media with increasing salt concentrations.

Time passed since isolation	Percentage of NaCl in medium				
	0	3/4	1 1/2	2 1/4	3
Strain *p* (258 days)	397	325	200	87	40
„ *q* (96 „)	382	397	242	72	42
„ *r* (45 „)	351	390	290	212	90
„ *s* (45 „	340	481	496	375	160

It is obvious from these observations that the longer the time the strain has been kept in pure culture the smaller is its adaptive power.

Quite the same phenomenon results from corresponding observations with *V. aestuarii*, as appears from Table IV.

Here too we observe that the longer the time which has elapsed since the isolation the smaller is the ability of the strain to adapt itself to unusual conditions. In other words the pure cultures of the bacteria under consideration are differentiated from the species as it occurs in nature by the loss of power to adapt themselves to sudden changes in environment. The longer the cultivation is continued the more this loss is accentuated so that by prolonged cultivation under constant conditions organisms result which might be called physiological artefacts.

TABLE IV.

Relation between the age of culture of various strains of *V. aestuarii* and their ability to grow in media with decreasing salt concentrations.

Time passed since isolation	Percentage of NaCl in medium			
	0	1	2	3
strain p (570 days)	23	37	82	430
„ q (360 „)	36	46	187	422
„ r (20 „)	52	130	340	441

§ 4. *Other presumable instances of physiological artefacts.*

Anyone who has given due attention to the remarkable results obtained by JAN SMIT in his study of the distribution of *Sarcina ventriculi* in nature [1]) will be struck by the great similarity between these dates and those presented in the foregoing paragraphs. Here again we meet with a bacterium which can be isolated according to the method given by BEIJERINCK from nearly every sample of soil. Still pure cultures of this bacterium mixed with sterilized samples of the same soils die quite rapidly, as may be inferred from the impossibility to reisolate after a very short time the organism out of the inoculated, previously sterilized, soil. Here again we are forced to conclude that an organism with the set of properties characteristic for *S. ventriculi* does not exist in nature. On the contrary it seems quite probable that this species is produced again out of a more or less common soil microbe under the special conditions of the enrichment culture: complete anaerobiosis and an extreme degree of acidity in the medium.

This view is not invalidated by the negative results of SMIT's experiments in which he tested several pure cultures of bacteria out of a "fertile" soil sample, on their ability to grow in the extremely acid, anaerobic enrichment medium. Again we must realize that the simple act of bringing the tested bacteria into pure culture will have damaged their adaptive power to a marked degree.

Finally we wish to draw the attention to some observations made by miss L. HOMANS in our laboratory. In studying the fermentability of "glutose" [2]) by bacteria miss HOMANS observed that from all soil samples tested a bacterium could be isolated which fermented glutose quite readily. This bacterium which proved to belong to the natural group of butyric acid bacteria, has received the provisional name of *Clostridium glutosicum* [3]).

[1]) JAN SMIT. Die Gärungssarzinen, Jena, 1930.

[2]) The rather vaguely characterized product resulting from the conversion of glucose and fructose in weakly alkaline media. Cf. W. COLTOF, Biochem. Zeitschr. **243**, 191, 1931.

[3]) An extensive report of the investigation of Miss HOMANS will appear later.

Now again it was most remarkable that from about 20 strains of the genus *Clostridium*, which had been isolated for the greater part from the same garden soil, none proved to be capable of fermenting glutose, even when cultivated in a suitable medium which contained a mixture of glucose and glutose. Since it seems excluded that ordinary garden soil will ever contain glutose, the occurrence of a special glutose fermenting bacterium in soil seems most improbable. Here again it appears much more likely that *Cl. glutosicum* is produced under the conditions of the enrichment culture from an ordinary butyric acid bacterium occurring in soil, which bacterium however looses its power of adaptation after being brought into pure culture in a glutose free medium.

In conclusion we wish to state explicitly that the views expounded above bear only a superficial resemblance to the theory forwarded by BEIJERINCK in his paper on the formation of physiological species. Whilst BEIJERINCK [1]) treated of irreversible changes of *pure cultures* of bacteria in answer to sudden changes in nutrient media, it seems to us that the adaptive power to sudden changes is restricted to the organisms as occurring in nature. The cultivation under ordinary laboratory conditions leads to an one-sidedness in properties which is most harmful to the adaptive power of the bacteria and which makes undoubtedly many of our pure cultures worthy of the name of physiological artefacts.

Laboratory for Microbiology of the Technical University.

Delft, March 31, 1932.

[1]) M. W. BEIJERINCK, These Proceedings, **16**, 1211, 1913.

Chemistry. — *Der Einfluss der Korngrösse von Stoffen auf deren Schmelztemperatur.* Von N. SCHOORL. (Communicated by Prof. ERNST COHEN.)

(Communicated at the meeting of April 2, 1932.)

Vor längerer Zeit (1909—1910) wurde seitens PAWLOW [1]) die Aufmerksamkeit auf die Erscheinung gelenkt, dass von verschiedenen Stoffen kleine Teilchen bei niedrigerer Temperatur schmelzen als grössere Kristalle. Er beschreibt u.a. folgenden einfachen Versuch: wird die Versuchssubtanz auf die Innenwand eines Glasrohres zerstäubt, so zeigen die feinsten Teilchen an der Glaswand einen tieferen Schmelzpunkt als

[1]) PAWLOW, Z. physik Chem. **65**, 1 (1909); **65**, 545 (1909); **68**, 316 (1910); **74**, 562 (1910).

die übrige Substanz, z.B. beim Salol um 7°, beim Antipyrin um 5° und beim Phenacetin um 4°. Er erklärt diese Erscheinung thermodynamisch dadurch, dass die Differenz in Oberflächenenergie zwischen der festen und der geschmolzenen Substanz sich ändert mit der spezifischen Oberfläche der festen Substanz. Beim Salol stellte er fest, dass bei hundertfacher Vergrösserung der spezifischen Oberfläche der Schmelzpunkt um 2,8° erniedrigt wird.

F. MEISSNER [1]) bestritt die genannte Beobachtung PAWLOW's ; derselbe bewies auf thermodynamischer Grundlage, dass das Gebiet, in welchem der Einfluss der Korngrösse auf den Schmelzpunkt sich beobachten lassen müsste, bei weit geringeren Dimensionen liegt, als die, welche in PAWLOW's Versuchen eine Rolle spielen.

Ich bin nunmehr der Meinung, dass zwar die Beobachtungen PAWLOW's an sich richtig sein können, dass dieselben aber anders zu deuten sind. Er arbeitete nämlich u.a. mit dem feinen Kristallpulver der untersuchten Substanzen in einem Glasrohr (siehe oben) bezw. auf einem Objektglas und stellte die Erniedrigung der Schmeltztemperatur unter dem Mikroskop fest.

Bringt man eine geringe Menge einer zerpulverten, kristallinischen Substanz in ein s.g. kapillares Schmelzrohr aus gewöhnlichem Glas und ermittelt durch erwärmen in einem Flüssigkeitsbade bei langsam ansteigender Temperatur den Schmelzpunkt, so lässt sich häufig die von PAWLOW beschriebene Erscheinung beobachten, falls man mittels einer starken Loupe oder eines schwach vergrössernden Mikroskops das Schmelzen der feinsten Teilchen beobachtet, welche sich an der Wand des Röhrchens festgesetzt haben. Man sieht dann, dass diese Teilchen um einige Grade tiefer schmelzen als die grösseren Kristalle, welche nicht unmittelbar oder nicht so innig mit der Glaswand in Berührung sind.

In dieser Weise vorgehend, habe ich am Veronal (Diäthylbarbitursäure), Luminal (Phenyläthylbarbitursäure), Antipyrin und Pyramidon (Dimethylamidoantipyrin) Unterschiede in der Schmelztemperatur bis 10 Grad beobachtet.

Anfangs glaubte ich, dass die für die feinsten Teilchen beobachtete niedrigste Schmelztemperatur die richtige wäre und dass die grösseren Teilchen zu hoch schmolzen infolge ungenügenden Kontaktes mit der Glaswand. Hiergegen spricht indes, dass der niedrigere Schmelzpunkt der feinsten Teilchen nicht übereinstimmt mit dem in der Literatur angegebenen Schmelzpunkt der betreffenden Substanz und dass der Schmelzpunkt der gröberen Teilchen viel mehr demjenigen entspricht, den man erhält, falls man die Schmelztemperatur mit dem Thermometer in der Schmelze ermittelt.

Ich habe nun gefunden, dass falls man Schmelzröhrchen aus Jenaglas verwendet, welches zuvor durch Spülen mit Wasser gereinigt war,

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[1]) F. MEISSNER, Z. anorg. und allgem. Chem. **110**, 169 (1920).

sich bei obengenannten Stoffen irgend ein Unterschied zwischen den Schmelzpunkten der feinen Teilchen an der Wand und den gröberen Teilchen gar nicht beobachten lässt. Auch erstgenannte zeigen dann den richtigen Schmelzpunkt und zwar äusserst scharf, falls man den Vorgang mit bewaffnetem Auge beobachtet, was bei genauen Schmelzpunktsbestimmungen einen grossen Vorteil bietet. Die Annahme liegt somit auf der Hand, dass bei älteren, etwas entglasten Schmelzpunktsröhrchen (wie dieselben bei den ersten Versuchen zur Verwendung kamen), die Entglasungsprodukte (Alkalikarbonate) des Glases durch Berührung mit den daran haftenden feinsten Kriställchen, eine Schmelzpunktserniedrigung erzeugen.

Dem entsprach folgende Beobachtung an sehr reinem (mehrmals aus Alkohol kristallisiertem) Mannit. In einem älteren, entglasten Röhrchen liess sich bereits bei 150° mittels eines schwach vergrössernden Mikroskops beobachten, dass die feinsten Kriställchen sich als kleine Tropfen an der Glaswand absetzten. Bei 160° hatten sich viele Tropfen gebildet und bei 165°.5 wurde der Endschmelzpunkt beobachtet. Als sodann ein neues Schmelzröhrchen aus demselben, aber vorher gereinigten, Glase verwendet wurde, ergab sich die Schmelztemperatur sämtlicher Kriställchen scharf zu 165°.8.

Ferner stellte sich heraus, dass noch ein zweiter Umstand bei der von PAWLOW beschriebenen Erscheinung eine Rolle spielen kann. An einem Handelsprodukt von Benzoin zeigten in einem neuen Schmelzröhrchen, aus vorher gereinigtem Glase, die feinen Teilchen einen Anfangsschmelzpunkt von 120°, während der Endschmelzpunkt der gröberen Kristalle sich zu 130°.5 ergab.

Nachdem dieses Präparat durch dreimaliges Umkristallisieren aus Alkohol gereinigt war, war die genannte Differenz zwischen den Schmelzpunkten verschwunden: sowohl die feinen Kristalle an der Glaswand wie die grösseren schmolzen bei 129°.5—133°.5. Hier wurde die PAWLOW'sche Erscheinung also wahrscheinlich hervorgerufen durch die in dem Handelspräparat vorhandene Verunreinigung, wobei die verunreinigende, den Schmelzpunkt erniedrigende, Substanz an der Oberfläche der Kristalle in Form eingetrockneter Mutterlauge vorhanden war, sich zunächst in feinen Stäubchen davon ablöst und dann, auf der Glaswand geklebt, den tieferen Schmelzpunkt hervorbringt.

Pharmazeutisches Laboratorium der Reichs-Universität.

Utrecht, März 1932.

Geology. — *The Rudist Fauna of Seroe Teintje Limestone (Northern Curaçao).* By H. J. MAC GILLAVRY. (Communicated by Prof. L. RUTTEN.)

(Communicated at the meeting of April 2, 1932.)

Rudist bearing limestone has been known for a long time to occur in Curaçao. Yet no good specimina had been secured. The material thus far collected consisted of shell fragments only, not permitting any exact determination of species or a fortiori of stratigraphical age. The age was inferred from the geological position and palaeontologically from the corals found together with rudists. At the end of this article I shall find occasion to discuss the age question more in detail.

Rudist fragments from Curaçao were first described by MARTIN (9, p. 239) as Dania curasavica, in 1885. In 1886 and again 1888 MARTIN (10, p. 238—240; 11, p. 21—26) recognized their real nature. According to BAILEY WILLIS (19, p. 639) STANTON on the base of MARTIN's illustrations identified them as of upper cretaceous age. Later the botanist BOLDINGH cursorily collected some material deposited in the collections of the Geological Institute of Utrecht. MOLENGRAAFF in his dissertation 1929 (12, p. 23) gives a good exposé of the stratigraphical relations, and, basing himself on GERTH's determinations of corals (5, p. 5), considers the Seroe Teintje limestone to be of lower senonian age. And thus the question remained unsolved, until ampler material should have been collected. With this end in view, during the excursion made by Prof. RUTTEN and some of his students of the university of Utrecht in 1930, the small mountain of Seroe Teintje was explored for a whole day, and not without success. The quality of the material thus collected compares remarkably well with that of other rudist material known from the West-Indies. Moreover we were lucky too in finding, besides Radiolite fragments, some Hippurite specimina not yet known to occur in Curaçao. Some of these even retained their superior valves. This probably is the second time superior valves of Hippurites have been found in America. [1])

Sometimes the fragments are rounded off and often much corroded. Moreover two Radiolite specimina were found to grow upon each other in the most irregular fashion, one growing almost diametrically opposite to the direction in which the other must have grown. In the interior cavity of one of these another Radiolite has grown concentrically with this one and in the same direction (Pl. II, fig. 6). This suggests that at the time

1) C.f. F. K. G. MÜLLERRIED. Anales del Inst. de Biologia. Mexico. T. I. N°. 2, p. 169, ? 1931.

of their occurrence the surge threw them together. This agrees with their low and spreading shape suggesting too the action of the surf upon them.

The material was collected at five localities known to, and mapped by MOLENGRAAFF. The bulk of the material including Nos. 1, 2 and 3 of the Vaccinites were actually found at Seroe Teintje. Vaccinites Nos. 4 and 5 were gathered from the Seroe Bomba Boea 400 m. N. 75 E. from the triangulation point 41. A few Radiolite fragments were found here too. Some material was also collected from the Seroe Hoba near Seroe Teintje. One Radiolite fragment was picked up on a small limestone hill 800 m. N. 62 W. from the "Landhuis Savonet". And finally some Radiolite fragments were collected on the most northern outcrops 700 m. N. 75 E. from the San Pedro church, Westpunt.

Besides rudists we found many corals and some Actaeonellae. The corals have been examined by Prof. H. GERTH. The material did not contain any species, not yet known from Curaçao. The Actaeonellae are ill-preserved; I was, in consequence, not able to identify them.

I wish to thank Mr. G. ASTRE, of Toulouse, and Mr. CH. T. TRECHMANN, of Castle Eden, who kindly gave their valuable advice about some specimina.

Vaccinites Martini. n. sp. (Pl. 1, fig. 1—6; text fig. 1, 2).

Inclination of dental apparatus . . . . . 20° (30°)
Space of circumference occupied by the three infoldings . 1/5 (1/7)
Pores not very well visible.

Quality of the material:

Five specimina were found, of which numbers 1, 2 and 3 were sawn through horizontally to enable examination of the transverse sections. One was sawn through vertically (N°. 4). The superior valves are either much corroded or covered by foreign substance and particles of limestone adhering very closely to them. This is the reason why the pores are not well visible. The inferior valves are much corroded too, only Nos. 1 & 2 showing the outside decoration.

Shape and external features:

The animal has the shape of a cone spreading upwards rather broadly, the top angle being about 70 degrees! Numbers 2 & 5 present an asymmetrical cone, but since in N°. 5 the steeper side of the cone corresponds to the dorsal (ligamental) side, while in N°. 2 just the reverse is the case, this seems not to be of any importance.

The superior valve is nearly a flat disc.

The sections are somewhat elliptical with the longer axis going from the anterior to the posterior side, the short one running dorsi-ventral.

The decoration of the outer surface consists of regular rounded, longi-

Fig. 1.

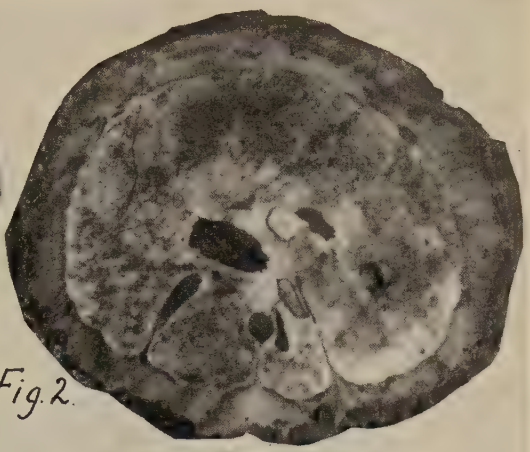


Fig. 2.

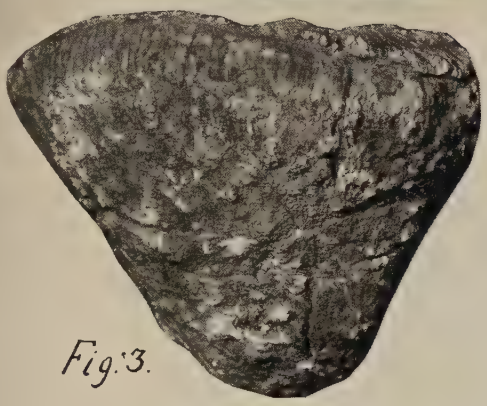


Fig. 3.

Fig. 4.

Fig. 5.

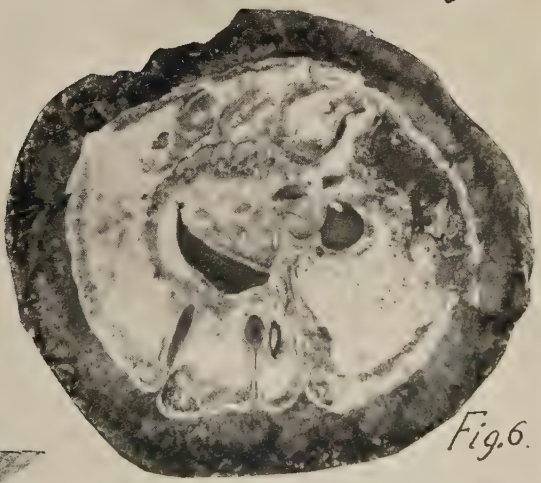


Fig. 6.

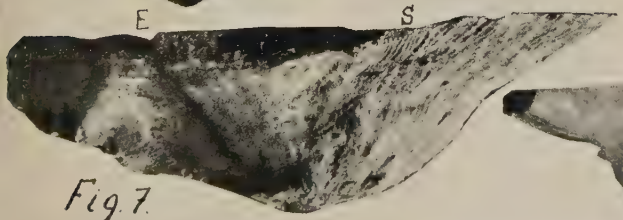


Fig. 7.

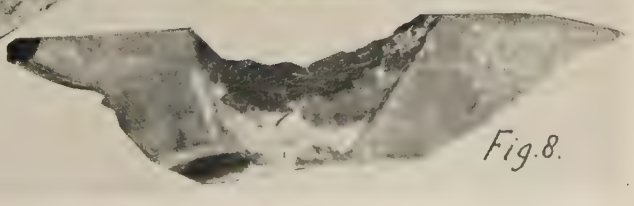


Fig. 8.

tudinal ribs, some 2 mm. broad and separated by shallow sulci equally broad and rounded. Occasionally these ribs bifurcate. The three grooves corresponding with the ligamental crest and the two pillars are rather shallow too. (Pl. I, fig. 1, L. S. E.) Yet they are deeper than the sulci above-mentioned.

Measures of holotype:

Diameter of the whole animal at the top: 110 by 95 mm. As preserved, it is 52 mm. high. When complete, it must have been about 70 mm. high. The thickness of the outer shell is about 10 mm. The animal being rather variable these measures of course have no absolute value.

Internal features:

The radial canals of the upper valve are very regular, a characteristic mentioned by TOUCAS (17, p. 89) for the younger groups of Vaccinites. The disposition of the dental apparatus is quite normal. The anterior tooth *(B')* is situated on the prolongation of the ligamental crest. The posterior tooth *(B)* lies directly behind the end of this crest. The posterior myophore *(mp)* lying on the same line with the two teeth, is situated directly alongside the first pillar, not going beyond its termination. This line makes the above-mentioned angle of 20° with the ligamental crest. The ligamental crest *(L)* is long and lamelliform and remarkably thin, being only half a mm. broad in the middle and one mm. at the top. Its length is 25—30 mm. The end is rounded thus marking a later evolutional phase (cf. TOUCAS 17, p. 69). The first pillar *(S)* is well pinched at the base over more than half its length. The end is knob-shaped with a diameter of about 5 by 7 mm. Its length is 15—20 mm. The second pillar *(E)* is pinched too at the base

Fig. 1 *Vaccinites Marlini.* *Fig. 2 (Holotype)*

Fig. 1 is the same as Pl. I, fig. 6; Fig. 2 is the same as Pl. I, fig. 2.
L: Ligamental crest; S: First pillar; E: Second Pillar; B: Posterior tooth; B': Anterior tooth; mp: Posterior myophore; ma: Anterior myophore; N: Single tooth of the lower valve; D: Living cavity.

but only over 3 or 4 mm. Then it broadens rather abruptly to a width of 4 mm. retaining this width over 15 mm., the rest of its length, the whole length thus being 20 mm. The outlines of the single tooth *(N)* of the lower valve, as well as those of the anterior muscle *(ma)* and mostly, also those of the accessory and the living cavity *(O & D)*, are very indistinct.

Variations:

Specimen N°. 3 differs from the others in two respects: Though much corroded this much can be said about its form, that it must have been more cylindrical than the others. Further the angle of inclination of the dental apparatus is 30° (Pl. I, fig. 5).

N°. 2 again differs, since the three pillars contain between them only $^1/_7$ of the whole circumference (Pl. I, fig. 6; text fig. 1).

I took N°. 1 for holotype because it agrees in most of the features with most of the others (Pl. I, fig. 1, 2; text fig. 2).

This species I have named in honour of Prof. Dr. K. MARTIN.

Systematical place:

The sum of the characteristics show the relation of this Vaccinites to either group I 4 (group of Vaccinites giganteus), or to group II (group of Vaccinites inaequicostatus) of TOUCAS (17, p. 89 and 104). The pores only might have given decisive evidence. But in this case, since pores must be very well visible to enable discerning between reticulate *(I)* and subreticulate pores *(II)* (a very subtle difference!) we can only rely on the internal features. But these do not differ very much. TOUCAS even regards group II as derived from Vaccinites praegiganteus. ASTRE, who kindly examined one of the sections, places this Hippurite in the group of Vaccinites inaequicostatus, on account of its ligamental crest being too thin for the group of Vaccinites giganteus. He gives the determination: Vaccinites cf. Oppeli Douv. I generally agree with ASTRE, but I should like to make it a new species since it differs from Vaccinites Oppeli in several respects. First it differs in the peculiar form of the second pillar, the long stretch over which the first pillar is pinched, the length and thinness of the ligamental crest, and secondly it differs because the posterior myophore is not advanced to the interior, a characteristic given by TOUCAS (17, p. 105) for this group. Now all these features certainly are quite variable, but all the same TOUCAS' system is based on them, while moreover in my specimina they appear to be very constant. Further TOUCAS (17, p. 110) considers Vaccinites Oppeli to be only a variation of Vaccinites inaequicostatus, which my Hippurite certainly does not resemble in the least.

It may be observed that the pillars of this Vaccinites bear great likeness to those of Barrettia monilifera. But this can be considered as a mere coincidence or perhaps a convergence.

Durania curasavica (MARTIN) (Pl. I, fig. 7, 8; Pl. II, fig. 1—6; text fig. 3, 4, 5).

Some literature on comparable forms:

1833	Hippurites Mortoni	8	Mantell	p. 130.
1836	Coniae sp.	7	Lyell in Huds.	p. 104.
1838	Hippurites Mortoni	6	Gray	p. 228.
1849	Hippurites Austinensis	15	Roemer	p. 410.
1850	Hippurites Mortoni	4	Dixon	p. 354. Pl. XXVI.
1852	Radiolites Austinensis	16	Roemer	p. 77. Pl. VI, fig. 1a—d.
1855	Radiolites Mortoni	20	Woodward	p. 59, 60. Pl. V, fig. 1, 2.
	= Sauvagesia austinensis: Toucas 18, 1909,			p. 96, 97, fig. 64.
1866	Radiolites Mortoni	21	Zittel	p. 148. Pl. XXV, fig. 1—3.
	= Sauvagesia austinensis: Toucas 18, 1909,			p. 96, 97.
1885	Dania curasavica	9	Martin	p. 239, 240 (1 text fig.).
1886	Radiolites sp.	10	Martin	p. 238—240.
1888	Radiolites sp.	11	Martin	p. 21—26. Pl. II, fig. 14—21.
1900 (1901)	Sphaerulites Mortoni	14	Parona	p. 15, 16. Pl. II, fig. 3a, b, 4.
	= Radiolites Paronai Dainelli 1901 (vide et Parona 1911).			
	= (fig. 3a, b). Sauvagesia austinensis: Toucas 18, 1909,			p. 96, 97.
1906	Radiolites Austinensis	1	Boese	p. 57, 58. Pl. XI, fig. 1; Pl. XIII, fig. 8; Pl. XIV, fig. 1.
1909 (1910)	Sauvagesia austinensis	18	Toucas	p. 96, 97, fig. 64.
	Sauvagesia Mortoni	18	Toucas	p. 92, fig. 59.
1912	Radiolites sp.	19	Willis	p. 639.
1929	Radiolites sp.	12	Molengraaff	p. 23.

Quality of the material:

Most fragments found belong to the group of the Radiolitidae as is evident from the structure of the shell, typical for this group. The combination of funnel plates (PALMER 13, p. 13, 76) and prismas, which constitute the shell, cannot be confused nowadays with any other structure. Moreover the irregular polygonal form of the prismatic cells in all the fragments makes it probable that they belong to the group of Sauvagésinés, (DOUVILLÉ 2, p. 15, 16), though other Radiolites were found to have the same structure. Most pieces are much too fragmentary to say anything about their systematical place. Nor can one be sure whether they belong all to the same species, since they show great variability in size, thickness of the funnel plates (= length of prismatic cells), etc. Some fragments show the prismatic cells to be high rather than wide, while others display just the reverse. Mostly the thickplated ones belong to very small, and perhaps cylindrical forms, but that is all very uncertain. Luckily better fragments were also found by us, showing parts of the internal cavity, or fragments of the outer, cortical layer, with its decoration; one retains its dental apparatus, while in others even the siphonal bands are shown. The latter allow some farther investigation. Only one individual shows, what I take to be a part of the superior valve. I figured it on Pl. II, fig. 5, so that everybody can judge for himself.

I will now describe the only rather complete specimen found, showing the whole circumference of the lower valve with the cortex for the greater part intact. One siphonal band is well preserved, the other however somewhat corroded. Probably only the lower end of the inferior valve is preserved, perhaps it is almost the whole inferior valve. One only thing to be said with any certainty is that the superior valve is wanting.

Some features not so well developed in this holotype and evident in other fragments will be described from these fragments, as it is highly probable that these belong to the same species.

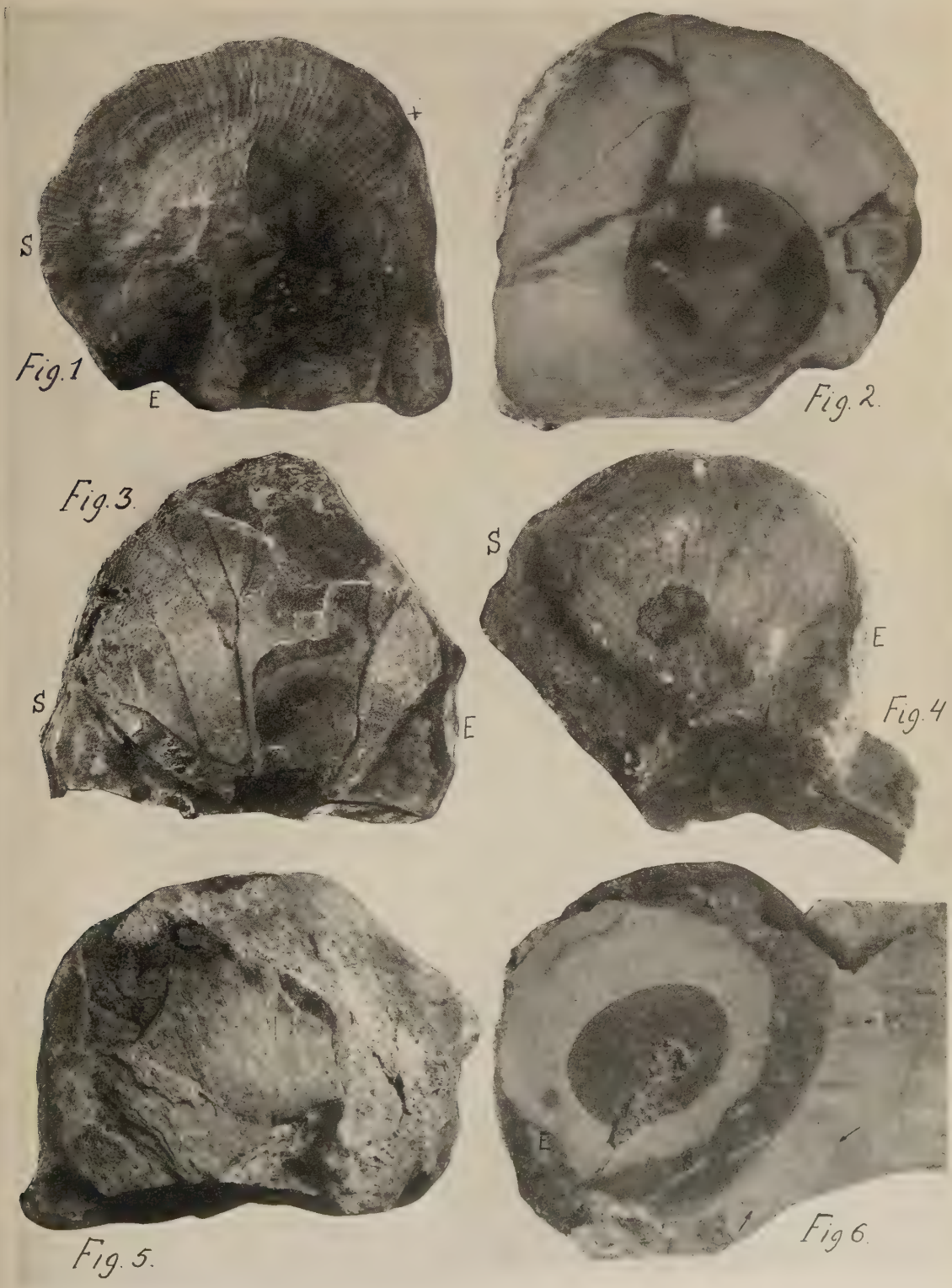
Description of holotype (Pl. I, fig. 7; Pl. II, fig. 1, 2; text fig. 5). As already stated, the holotype lacks its superior valve.

External features:

The shape is that of a very flat cone, Lapeirousia and Sphaerulites-like. This is very exceptional for Sauvagesia and Durania. Thus TRECHMANN in a letter written to me about it even thought of the possibility of constituting a new genus for it. I do not think, however, that my material would justify this, as, the upper valve absent, it is not absolutely complete. The cortical decoration consists of more or less regular longitudinal, rounded ribs, 2 mm. broad. They are separated by shallow rounded sulci. On about one fourth of the circumference, on the dorsal, ligamental side, these ribs and sulci are of a complex nature, showing small secondary ribs and sulci; sometimes in a wide primary sulcus three secondary ribs can be found (Pl. II, fig. 1). The two siphonal bands are well marked. The anterior band *(E)* is a channel rather deeply concave. Though much marred by corrosion some remnants of minor ribs can be traced. At this place the shell is at its thinnest. From the two borders of this anterior siphonal channel, the shell becomes thicker and thicker, the circumference running outwards at a tangent. When a certain thickness of shell is attained the circumference of the shell follows almost concentrically the inner cavity. The longitudinal band between the two siphonal areas is simply rounded. Its ornamentation is corroded away, but traces of it show that it probably consisted of common, larger ribs, not comparable to those of the siphonal areas. The posterior area (*S*) is well preserved. It is scarcely concave and is ornamented with rounded single minor ribs, about fifteen in number. The width of the two areas is almost alike. The anterior channel is 16 mm. wide, the posterior one 13 mm., both measured at the top.

Measures:

Diameter of the whole animal at the top: 135 by 115 mm. The inner cavity is 56 by 60 mm. The outer shell is 5 mm. thick at the anterior siphonal area, and 50 at the opposite, dorsal side. The thickness of the inner shell layer is less than 1 mm. As preserved, the lower valve is 38 mm. high. The value of these measures of course is very relative, as this species must have varied considerably both in size and shape.


S
E
Fig. 1
Fig. 2
Fig. 3
S
E
S
E
Fig. 4
Fig. 5
E
Fig 6

The structure of the shell:

The funnel plates or growth layers, are very thin: 0,4—0,7 mm. They are coarsely cellular. The cells are polygonal. The prismas are rather wide, their diameter being often about 1 mm. Thus their diameter is greater than their height. This is at least the case in the type specimen. Other fragments show all sorts of nuances, up to prismas with a height twice the width, but it is questionable whether these belong to the same species, their general appearance being somewhat different, as I already stated.

The radial and bifurcating vessel impressions are often very conspicuous (Pl. II, fig. 3). In cross-sections they appear as small denticles reaching from one funnel plate into the next. This resembles the feature given by DOUVILLÉ (3, p. 56) for Parabournonia as represented by his fig. 2b. Thus these denticles of Parabournonia could perhaps be explained in this way, and then of course would constitute no generic characteristic at all.

The funnel plates as a rule are wholly destitute of any undulations, and appear to have been deposited horizontally one upon the other, spreading downwards rather than upwards. Only in the two siphonal areas there are shallow, flat-bottomed, but steep-edged depressions. Thus these depressions are more or less trough-shaped. This is shown in cross-sections, because these edges betray themselves, by a radial arrangement of the funnel plate lines. Moreover as a sequel of this steepness these lines pack closely together. Thus here the shell structure seems to be more opaque [1]). The two opaque lines thus formed are as a rule more distant from each other at the inner side of the outer shell than at its outer (Pl. II, fig. 6; text fig. 5). These depressions are reminiscent of those of Tampsia (Proc. U. S. Nat. Mus. 61, 1922, p. 7).

A regular but small undulation of the growth layers is only to be found near the cortex, where the ribs begin to be marked.

The inner shell layer is very thin and opaque.

Internal features:

The circumference of the inner cavity shows no trace of a ligamental crest or inflexion. It is approximately circular showing only a slight flattening of the border line on the places corresponding to the two siphonal areas. The fig. 2, Pl. II, will show two patches of white crystalline calcite in the inner cavity on the dorsal side. Probably these are the lower ends of the two teeth of the upper valve, though they appear to be situated rather far away from the border.

Characteristics shown in other fragments:

Some features shown in other fragments better than in the holotype, but which could be traced to occur in this also, have already been described. I shall now give the features shown in other fragments only.

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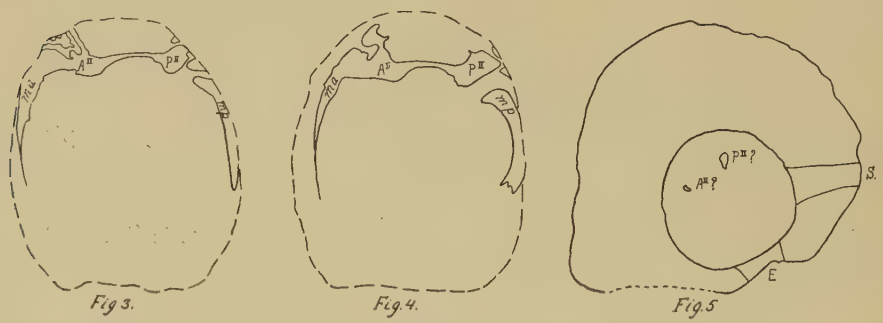
[1]) This, then, very much resembles DOUVILLÉ's characteristic for „Sauvagésinées" (2), so that perhaps this also might be explained out of the shell structure.

One fragment has its dental apparatus very well preserved (text fig. 3, 4). This bears a typical Radiolite character, and is almost identical with that figured by TOUCAS (17, p. 92, fig. 59) of Sauvagesia (Durania) Mortoni.



Durania Curasavica.

Fig. 3 and 4: Two sections through the inner cavity of the fragment with preserved dental apparatus. Fig. 5 is the same as Pl. II, fig. 2.

AII: Anterior tooth; PII: Posterior tooth; ma: anterior myophore; mp: posterior myophore; E: Anterior siphonal channel; S: Posterior siphonal band.

To the right of PII in fig. 3 and 4 the two ridges forming one of the two grooves serving as a sort of slot for the dental apparatus are visible.

Fig. 3 is a lower section than fig. 4.

In fig. 5 the opaque lines limiting the two trough-shaped siphonal depressions of the funnel-plates have been indicated.

This fragment resembles the holotype in shell-structure, form of inner cavity, decoration of the outer shell surface, etc. Thus I take it to belong to the same species as the type exemplar, and therefore this dental apparatus to be typical of the species.

One most peculiar individual has been found that shows in the wall of the interior cavity the existence of Lapeirousia-like pseudopillars. The funnel plates moreover are more foliaceous. Thus this specimen might be a Lapeirousia. The general bearing however does not differ much from that of the Durania fragments. The cortex is not preserved. This is greatly to be pitied, because now nothing decisive can be said about this animal.

Systematical place:

It will be clear, that this species bears a remarkable resemblance to Durania Mortoni found in the south of England, and to the Durania austinensis first found by ROEMER in Texas. Thus my description of it as a new species under the name originally given by MARTIN to the Curaçaoan fragments, will need some justification.

MANTELL in 1833 (8, p. 130) only names, not describes Hippurites Mortoni. ROEMER in 1849 and 1852 gives only a very insufficient description of a very insufficient fragment found near Austin, and names it Hippurites austinensis (15, p. 410; 16, p. 77). Later more rudists found in Europe have been compared with Durania Mortoni or austinensis and were named

accordingly by their authors. Moreover these two species were considered as identical, for instance by ZITTEL (21, p. 148). TOUCAS divided the material then found, again in two groups. Some fragments are identified by him as Sauvagesia Mortoni others as Sauvagesia austinensis. But certainly these fragments are mostly not good enough to permit this. Thus for example PARONA's fragment, or ZITTEL's (14, Pl. II, fig. 3a, b; 21, Pl. XXV, fig. 1). Moreover all these descriptions leave so much room for different interpretation that for instance TOUCAS (17, p. 97) states that Sauvagesia austinensis has no trace of a ligamental inflexion where BOESE (1, p. 57) assures us that it certainly has. The TOUCAS article appeared 3 years after that of BOESE, but TOUCAS does not mention BOESE at all. Yet some comment in so important a question clearly could be expected. Moreover the only difference to be found in TOUCAS' descriptions between Mortoni and austinensis (17, p. 92 and 96) appears to be the age of the strata in whiuh they were found.

Thus my material although incomplete too as regards the absence of the superior valves, seems to justify my describing it as a new species. The name austinensis will have to disappear from literature until a good specimen is found near Austin in the Austin chalk. Even then it will be questionable if it will not be better to give a new name than to keep the old one which has caused so much confusion.

I choose for this species the specific name originally given by MARTIN to the first fragments found by him. Though later he himself when detecting the Radiolite nature of the material, dropped this name as of course was necessary on account of its fragmentary condition, this name may now be revived. Moreover if later other Radiolite species should be found in Curaçao, it does not matter to which of these the original name is given.

Localities:

The holotype as well as most of the material figured in this article was actually found at Seroe Teintje. Only the "interbande" fragment of Pl. II, fig. 3 was found at the outcrops near Westpunt.

Stratigraphical conclusions:

Finally the age question remains to be considered. Of the group of Vaccinites inaequicostatus according to TOUCAS all members up from Vaccinites CHAPERI have rounded ligamental crests. Vaccinites CHAPERI occurs in the European Santonian strata, while Vaccinites inaequicostatus, Oppeli and vesiculosus occur in the Campanian. In the group of Vaccinites giganteus, only Vaccinites giganteus and its var. major have rounded ligamental crests. Vaccinites giganteus occurs in the Coniacien, Vaccinites giganteus var. major in the Lower Santonian strata. For Durania austinensis TOUCAS gives upper Santonian age in England and likewise in Texas. TOUCAS gives

Ligerian (lower Cenomanian) age for one specimen of Durania Mortoni, while another has been found on the limit of the Turonian and Cenomanian strata. BOESE (1, p. 24) gives Lower Senonian age for the fauna, in which his fragments of the Radiolite, described by him as Radiolites austinensis were found (1, p. 57). As I have already stated, he says that one individual found by him clearly shows a ligamental crest, which would make it principially different from my material. Moreover this would point to an older age than Senonian. (DOUVILLÉ 2, p. 23). On the other hand his figure (1, Pl. XI, fig. 1) is not very convincing, and might easily represent one of the dental or adductory ridges which form a sort of slot for the dental apparatus. In a badly preserved specimen these easily might be mistaken for a somewhat reduced ligamental inflexion, as is shown by some of my fragments.

Everything considered the facts agree quite well with the Lower Senonian age given by GERTH on account of the corals.

A more precise determination of the age is difficult to obtain. The Vaccinites is of a young type. The only other American Vaccinites known is Vaccinites Sanchezi, found by SANCHEZ and described by DOUVILLÉ (3, p. 54). It occurs on Cuba in strata of Dordonian age according to DOUVILLÉ (3, p. 50), but it is entirely different from my species.

SUMMARY:

Two new rudists are described and named Vaccinites Martini n. sp. and Durania curasavica (MARTIN). Thus far this fauna is different from any other fauna known. The age certainly is Senonian, probably Campanian or even Maestrichtian.

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*) Indicates that I could not consult the article in question.

EXPLANATION OF PLATES.

PLATE I.

Fig. 1. Vaccinites Martini N°. 1. (Holotype). Seen from the posterior dorsal side. By L., S & E the three grooves corresponding with the ligamental crest and the two pillars are indicated. They are best shown directly beneath the section. × ¾.

Fig. 2. Same specimen. Section. For explanation of details see text rig. 2. × ²/₃.

Fig. 3. Same species N°. 5. Seen from the ventralside, so that the second pillar (E) is on the right. × ²/₃.

Fig. 4. Same specimen as in fig. 3, seen from above showing the superior valve. This upper valve is much corroded. Thus the pores cannot be seen. The radial canals are shown; likewise the ligamental crest and the two pillars, as the upper valve is worn away over them. L.: Ligamental crest. S.: first pillar. E.: second pillar. × ²/₃.

Fig. 5. Vaccinites Martini N°. 3. A more cylindrical form. The outer shell is corroded away on this side, so that the ligamental crest and the two pillars are shown. × ²/₃.

Fig. 6. Vaccinites Martini N°. 2. Individual, with pillars and ligamental crest closer together than in the others. For explanation of details see text fig. 1. × ²/₃.

Fig. 7. Durania curasavica (Martin). Holotype, seen from the posterior side. The concave anterior siphonal channel and the flat posterior siphonal band are well shown (E and S). × ²/₃.

Fig. 8. Durania curasavica (Martin). Vertical section of other individual. Showing the horizontal funnel plates and low prismas. × ⁴/₅.

PLATE II.

Fig. 1. Durania curasavica (Martin). Holotype. Seen from below. E.: anterior siphonal channel. S.: posterior siphonal band. On the "interbande" traces of common larger ribs are shown. From S to the cross, the ribs and sulci are complex as can be seen at several places. × ½.

Fig. 2. Durania curasavica (Martin). Holotype. Section. For explanation of details see text fig. 5. × 5/9.

Fig. 3. Durania curasavica? (Martin). "Interbande" fragment, showing cellular structure, bifurcating vessel impressions, and trough-shaped siphonal depressions of the funnel plates, S and E, as in fig. 1. × ¾.

Fig. 4. Durania curasavica (Martin). "Interbande" fragment showing the trough-shaped siphonal depressions of the funnel plates, S. and E., as in fig. 1. × 2/3.

Fig. 5. Durania curasavica? (Martin) with part of superior valve. The structure of this is not cellular and the much thinner plates are finely striated. × 4/7.

Fig. 6. Durania curasavica (Martin). Showing one individual growing in the interior cavity of another greater one. The two arrows point to the two opaque lines limiting one of the trough-shaped siphonal depressions. E. and S. as in Fig. 1. × 4/7.

Geology. — *Über die möglichen Ursachen der Undationen der Erdkruste.* Von R. W. VAN BEMMELEN. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated at the meeting of April 2, 1932.)

Von HAARMANN [1]) wurde eine bikausale Darstellung der Bodenbewegungen gegeben, welche von ihm als Oszillationstheorie bezeichnet wurde. In derselben wird unterschieden zwischen: *Primärtektogenese,* welche die vertikalen Bodenbewegungen umfasst, und *Sekundärtektogenese,* wozu gerechnet werden die sekundären Reaktionen, die Abgleitung und Zerrung im gehobenen Gebiete und Zusammenpackung, Faltung und Ueberschiebung im gesenkten Gebiete herbeiführen. Die vertikalen Bodenbewegungen wurden von HAARMANN *Oszillationen* genannt.

Es ist jedoch nicht möglich, mittels dieser Oszillationen alpine Deckenstrukturen mit Total-Ueberschiebungsbeträgen von Hunderten von Kilometern zu erklären. Dies würde die Annahme von Hebungen unwahrscheinlich grossen Ausmasses erheischen.

In einer Abhandlung über die Bikausalität der Bodenbewegungen [2]) legte ich jedoch dar, dass dieser Einwand gegen die Oszillationstheorie zu beseitigen wäre, wenn die primäre Bodenbewegung nicht schlechthin aufgefasst würde als vertikale Hebungen und Senkungen an bestimmtem Orte (Oszillationen), sondern ihr räumliches und zeitliches Verhalten zurückgeführt würde auf eine Wellenbewegung der Kruste, bei welcher der Wel-

[1]) Die Oszillationstheorie. Stuttgart 1930.

[2]) Nat. Tijdschr. v. Ned.-Indië. 3e afl. 1931. Auch: "Magma- und Krustenundationen, Verhand. v. h. VIe Natuurwet. Congr. Bandoeng, Sept. 1931.

lenkamm sich seitwärts (d.h. in der Richtung quer zu seiner Längserstreckung) fortbewegt. Diese Bewegung wurde von mir *Undation* genannt, und es wurde bemerkt, dass es vielleicht besser wäre, von *Undationstheorie* zu sprechen. Dieses Prinzip einer sich fortbewegenden Welle ist sehr wohl imstande zu erklären, wie Krustenmaterial in Form von Decken über grosse Abstände verfrachtet werden kann, ohne wesentlich grössere Höhendifferenzen im Erdrelief annehmen zu müssen als die gegenwärtig bekannten.

Auf die Ursache der Undationen wurde noch nicht eingegangen; diese Frage wollen wir jetzt erörtern.

HAARMANN sucht die Ursache der Oszillationen in Polverlegungen, welche Deformation des Erdellipsoids im Gefolge haben. Zur Gleichgewichtserneuerung sollten subkrustale Massenumlagerungen auftreten, die sich an der Oberfläche als vertikale Hebungen und Senkungen äussern würden.

Ich suche jedoch die Ursache in gänzlich anderer Richtung; nicht in kosmischen Kräften, sondern in einer Kraftquelle, die in der Erdkruste selbst auftritt, nämlich die *magmatische Differentiation* [1]).

Nach der modernen Seismologie (GUTENBERG, JEFFREYS) besteht die Erdkruste nicht aus zwei, sondern aus wenigstens drei Schichten. Die alte Darstellung, bei welcher einzig von Sial (Sal) und Sima gesprochen wird, ist folglich zu einfach, ebenso die Airy'sche Hypothese der isostatischen Kompensation. Ueber die Zusammensetzung der verschiedenen Schichten gibt es mehrere Hypothesen von DALY, JEFFREYS und HOLMES.

KRAUS [2]) hat hingewiesen auf das Wachstum der Kontinente durch fortgesetzte Differentiation eines Stammagmas, welches er Salsima nannte. Durch die Spaltung dieses wahrscheinlich gabbroiden Stammmagmas wird spezifisch leichteres Sal und spezifisch schwereres Sima neu gebildet. Dieser Prozess findet hauptsächlich während der orogenetischen Perioden statt und wird von vulkanischer Aktivität begleitet. Im Anfang der Orogenese (im Vortiefenstadium) sind die vulkanischen Produkte stark basisch, am Ende steigen saure, granitische Differenziate als Batholithe empor.

Das Salsima soll die Silikatschmelze sein, die ursprünglich infolge der Abkühlung der Erde erstarrte. Nachher wurde es unterkühlt und bildete den Boden der Urozeane, zu denen die alte Tethys und der gegenwärtige Pazifik, sowie möglicherweise ein Teil des gegenwärtigen Indik zu rechnen sind. Weiter ist dieses Stammagma auch in ausgedehnten Linsen unter den Kontinenten vorhanden, wo es die sogenannte intermediäre Schicht bildet. Die oberste, granitische Schicht entspricht dem alten Begriff des Sal, das schwere Substrat jenem des Sima.

Der Differentiationsprozess des unterkühlten Salsima findet fortwährend

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[1]) Eine Ausarbeitung der Undationstheorie nach diesem Prinzip, sowie eine Anwendung auf den westlichen Teil des Sundabogens, wird in kurzem erscheinen im Natuurk. Tijdschr. v. Ned.-Indië, (De Undatie-theorie, hare theoretische afleiding en hare toepassing op het westelijk deel der Soendaboog (mit 10 Textfiguren und englischer Zusammenfassung).

[2]) Das Wachstum der Kontinente nach der Zyklustheorie, Geol. Rundschau, 1928.

statt und zwar bereits seit dem frühesten Anfang der Erdgeschichte, als die Abkühlung des Salsima die Minimaltemperatur seines Existenzbereichs überschritt. Der Prozess hat auch jetzt noch kein Ende gefunden.

Die Spaltung des Stammagmas wird als Reaktion auf Abkühlung nach dem Prinzip LE CHATELIERS ein exothermer Prozess sein. Einmal in Gang gebracht, wird er nicht leicht beendet, doch breitet sich mit abwechselnden Perioden erhöhter und verringerter Aktivität im Stammagma aus.

Es verläuft überaus intensiv in den sog. Geosynklinalen, die demnach ein unruhiges Bodenrelief und grosse vulkanische Aktivität und Seismizität zeigen. *Die Geosynklinalen wären folglich zu definieren als Gebiete, wo der Differentiationsprozess des Stammagmas aktiv vor sich geht.*

Unabhängig von dieser Einteilung der Kruste in Schichten nach der Geschwindigkeit der Erdhebenwellen und nach der chemischen Zusammensetzung kann man auch *eine solche nach der Bewegungsmöglichkeit* des Materiales aufstellen.

VAN HISE[1]) unterscheidet eine oberste *Bruchzone* (zone of fracture) von 10—12 km Mächtigkeit, und unter ihr eine Fliesszone (zone of rock flowage), wo infolge der grossen Belastung der Druck einen hydrostatischen Charakter hat und der Widerstand der Gesteine sehr gering ist.

Eine Konsequenz der hydrostatischen Spannungsverteilung in der Fliesszone und des geringen Widerstandes der Gesteine gegen „Stress" ist, dass in dieser Zone auch *hydrostatisches* Gleichgewicht herrschen muss. Ein Ergebnis der Schwerkraftmessungen ist, dass die Erdkruste sich nahezu in *isostatischem* Gleichgewicht befindet. Dies ist jedoch eine *Minimal*forderung. Das Krustenmaterial wird auch *nach hydrostatischem Gleichgewicht streben.*

Wenn das Stammagma mit spez. Gew. 3.0 sich spaltet in salische Produkte mit spez. Gew. 2.8 und simatische mit spez. Gew. 3.2, so werden erstere sich an der Oberseite konzentrieren, letztere unten. Es bildet sich folglich in einer Zone aktiv verlaufender Aufteilung eine lokale Anhäufung von Sal und Sima. Das *Totalvolumen* braucht sich dabei nicht wesentlich zu ändern, das *Totalgewicht* bleibt konstant. Es ist also möglich, dass dieser Prozess im Untergrund vor sich geht, ohne dass *vertikale Bodenbewegungen auftreten und ohne dass das isostatische Gleichgewicht gestört wird.*

Das hydrostatische Gleichgewicht muss jedoch durch die Magmaspaltung gestört werden. Die Anhäufung salischer Zerlegungsprodukte ist *zu leicht* im Verhältnis zum umgebenden, noch undifferenzierten Stammagma, die Anhäufung der simatischen Produkte um gleichviel *zu schwer.* Infolgedessen wird die salische Masse empor-, die simatische seitwärts gedrückt[2]). Zwischen beide wird *frisches Salsima* injiziert. Dieses Salsima wird den Nachbargebieten entzogen, wodurch neben dem sich erhebenden

[1]) A treatise on Metamorphism, U. S. Geol. Survey Mon., XLVII, 1904.

[2]) Seitwärts, nicht abwärts, weil nur seitwärts Ausweichungsmöglichkeit besteht.

Geotumor *Vortiefen* entstehen. Weil Volumänderungen bei diesem Prozesse bedeutungslos sind, muss das Totalvolumen der Vortiefe unter dem ursprünglichen Niveau der Bodenoberfläche gleich dem Volumen der Aufwölbung oberhalb dieses Niveaus sein.

Diese hydrostatischen Ausgleichsbewegungen werden danach streben, so viel wie möglich *unter Einhaltung des isostatischen Gleichgewichts zu verlaufen*. Die Masse des dem Vortiefengebiet entzogenen Salsima wird im Untergrund isostatisch kompensiert durch eine Welle schweren simatischen Materials, welches aus dem Gebiete aktiver Magmaspaltung seitwärts fortgedrückt wird.

Die Simawelle befindet sich jedoch in einer Tiefe von einigen zehn Kilometern, wo die innere Reibung infolge des hohen hydrostatischen Drucks bereits verhältnismässig gross ist. Diese kompensierende Welle wird sich folglich *träger* bewegen, als die Entziehung des Salsima aus dem Nebengebiete erfolgt. Das hat zur Folge, dass Salsima aus einem breiteren Gebiete abfliesst, als im Untergrund durch die Simawelle isostatisch kompensiert wird. Hierdurch entsteht ein Streifen mit Massendefekt parallel zur Zone von welcher die Gleichgewichtsstörung ausgeht (sog. *Achse von* VENING MEINESZ[1]).)

Das Oberflächenrelief wird in erster Linie bestimmt durch die Mächtigkeit der Salkruste und kann deshalb *unabhängig* von der subkrustalen Gleichgewichtsstörung sein, wie auch mit der Achse von VENING MEINESZ der Fall ist.

In diesem Stadium der Aufwölbung und Vortiefe wird jedoch die Forderung hydrostatischen Gleichgewichts noch nicht erfüllt. Dies wird erst der Fall sein, wenn die drei Schichten (Sal, Salsima und Sima) überall gleiche Mächtigkeitsverteilung erreicht haben. Dies muss mit Injektion salischen Materials unter der Bruchzone der Vortiefe gepaart gehen, wodurch die Aufwölbung sich wieder senkt und der Boden der Vortiefe emporgedrückt wird.

Wenn jetzt der Differentiationsprozess des Stammagmas aufhörte, würde das Gleichgewicht in der Erdkruste so gut wie möglich wiederhergestellt sein. Weil jedoch die Aufteilung exotherm verläuft, wird sie weiter fortschreiten. In der ursprünglich aktiven Zone wird das neu injizierte Stammagma von ihr ergriffen. Von dieser Zone werden deshalb weiterhin Hebungsimpulse ausgehen. Infolge der Mächtigkeitszunahme der Sal- und Simaschichten und der damit zusammenhängenden Mächtigkeitsverringerung der Salsimaschicht nimmt die Intensität der Impulse ab.

Es gibt jedoch noch eine andere Art der Fortpflanzung des Spaltungsprozesses. Es wurde gezeigt, wie behufs Wiederherstellung des hydrostatischen Gleichgewichts dem Nachbargebiet Salsima entzogen wird. Wenn das Stammagma ursprünglich eine Schicht von 40 km Mächtigkeit bilde-

[1]) VENING MEINESZ, Maritime gravity survey in the Netherlands East Indies, tentative interpretation of provisional results. Proc. Kon. Akad. v. Wetensch. Amsterdam, Vol. XXXIII. Page 556, 1930.

te [1]), so wird dieselbe im Vortiefenstadium stark reduziert, z.B. auf 20 km. (An der Oberfläche äussert sich diese Mächtigkeitsabnahme nur durch eine Senkung im Betrage von einigen wenigen Kilometern, da sie im Untergrunde durch den Zufluss der Simawelle so gut wie möglich isostatisch kompensiert wird.) Die Folge dieses Dünnerwerdens der Salsimaschicht ist, dass Material, welches zuerst in einer Tiefe von 40 km unter dem Drucke der 40 km hohen Gesteinssäule mit spez. Gew. 3.0 lag, jetzt eine Druckentlastung von ca 6000 Atm. erfährt. Ausserdem ist die der Tiefe von 40 km entsprechende Geoisotherme von ca 1300° C. jetzt aufwärts ausgebogen bis in die Zone, wo normalerweise Geoisothermen von 600°—700° C. verlaufen. *Durch diese gewaltige Druckentlastung, verbunden mit einer relativen Temperaturerhöhung, sind in der Vortiefe die Bedingungen für das Einsetzen des Prozesses der fraktionierten Auskristallisierung günstig geworden.*

Zuerst war unter den vorherrschenden Druck- und Temperaturbedingungen die innere Reibung des Magmas so gross, dass die Diffusionsgeschwindigkeit der Moleküle und Ionen nahezu null war. Durch die Druckentlastung in der Vortiefe wird jedoch die innere Reibung geringer und der Auskristallisierungsprozess kann einsetzen.

Durch die damit verbundene Wärmeentwicklung greift der Prozess weiter um sich.

Das Ergebnis ist also *die Bildung einer neuen Zone magmatischer Differentiation parallel zur ursprünglichen Impulszone,* in welcher das hydrostatische Gleichgewicht gestört wird, und von welcher folglich Hebungsimpulse ausgehen.

Unter günstigen Bedingungen, wie sie in geosynklinalen Gebieten vorliegen, ist es möglich, *dass durch diese Seitwärtsverlegung des Differentiationsprozesses, die damit verbundene Hebung sich über grosse Entfernungen der Erdoberfläche entlang fortbewegt, ohne dabei an Intensität einzubüssen. Das sind die wellenförmigen Deformationen der Erdkruste, die Undationen, die alpine Deckenstrukturen zu erzeugen vermögen.* Durch die Sekundärtektogenese *schiebt sich* Krusten- und Sedimentmaterial in der Vortiefe *zusammen,* und durch die Wanderung der Aufwölbung wird das Deckenpaket *weitergeschoben.* Für die Einzelheiten einer derartigen Zusammenpackung nach der Undationstheorie darf auf die Beispiele in meiner Abhandlung über die Bikausalität der Bodenbewegungen (l.c.) verwiesen werden.

Dasjenige was wir an der Oberfläche beobachten, ist das Ergebnis der Interferenz zwischen *Impuls- und Wiederherstellungsfaktoren. Impulsfaktoren* sind:

1. Die *Geschwindigkeit,* mit welcher der Spaltungsprozess des Stammagmas vor sich geht.

[1]) Nach der Seismologie entspricht diese Zahl ungefähr der Dicke der Oberflächenschicht des Pazifiks (P. Byerly).

2. Die *Geschwindigkeit,* mit welcher dieser Prozess sich seitwärts verlegt.

3. Die *Mächtigkeit* der Stammagmaschicht.

4. Die *Ausdehnung* der Salsimaschicht und ihre *Begrenzung* durch bereits früher aufgeteilte Gebiete.

Wiederherstellungsfaktoren sind:

5. Die *Geschwindigkeit,* mit welcher sich das hydrostatische Gleichgewicht wiederherstellt.

6. Der *Grad* bis zu dem es sich wieder herstellt.

Die relative Grösse von 1 und 5 bedingt, ob Gelegenheit zur Bildung lokaler Anhäufungen salischer und simatischer Spaltungsprodukte besteht. Die relative Grösse von 2 und 5 bedingt, ob *plateauartige Aufwölbungen* oder *schmale, parallele Bergketten und Inselbogen* entstehen. Wechsel dieser Faktoren in der Richtung der Längsachse verursacht *Achsensenkung* und *-hebung* und *Virgationen der Ketten.*

Die Undationen breiten sich von ihrem Anfangspunkte aus wie Wellen von einem Zentrum, wo das Gleichgewicht der Wasserfläche gestört ist. Wenn, ausgehend von mehreren Zentren, die Undationsbogen einander begegnen, entsteht *Scharung* der Bogen.

Faktor 3 bestimmt ob die lokale Anhäufung von Spaltungsprodukten beim „Nachhinken" der hydrostatischen Gleichgewichtserneuerung gross oder klein ist. Davon wiederum hängt der Reliefunterschied ab, welcher im ersten Stadium der hydrostatischen Ausgleichsbewegungen entsteht, also, ob hohe Kettengebirge mit tiefen Vortiefen oder nur schwache Aufwölbungen und Depressionen gebildet werden. Ersteres wird sich vorzugsweise in den Geosynklinalen ereignen, wo das Stammagma noch mächtig ist, letzteres in kontinentalen Gebieten, wo das Magma bereits grösstenteils gespalten ist. Dies entspricht resp. den *orogenetischen* und den *epirogenetischen Bewegungen.*

Faktor 4 bewirkt eine Anpassung der Undationsbogen an das Vorland, da infolge der Mächtigkeitsabnahme der Salsimaschicht die Seitwärtsverlegung des Differentiationsprozesses gebremst wird. Auch das Sekundärtektogenetisch zusammengeschobene Deckenpaket wird vom Vorland in seiner Weiterbewegung gehemmt. Dadurch wird es vom Hebungsimpulse eingeholt und zum Gebirge erhoben. Die Magmaspaltung im Untergrund kann sich wegen der Bedeckung durch das mächtige Deckenpaket nicht als Vulkanismus an der Oberfläche äussern. Wohl steigen die salischen Spaltungsprodukte in der Aufwölbungsachse empor, weil dort Zerrung vorherrscht; das sind die sog. *postorogenetische Batholithe.*

Das Einholen des Deckenpakets vom Hebungsimpuls mag auch ein „Zurücksinken" der Decken-„Wurzeln", die sog. *„Rückfaltung",* verursachen.

Im allgemeinen erklärt diese Anpassung des Verlaufs der Undationsbogen und des von ihnen sekundärtektogenetisch zusammengeschobenen

Deckenpakets an das kontinentale Vorland die Erscheinung der *Rahmenfaltung*.

Infolge der Sekundärtektogenese wird die Kruste an der äusseren Seite des Undationsbogens verdickt, weil die Krustengesteine und Sedimentpakete in der Vortiefe zusammenschieben. Der Prozess der Magmaspaltung, welcher ursprünglich durch die Druckentlastung im Vortiefengebiet eingeleitet wurde und sich weiterhin exotherm entwickelt, wird hier zwar Hebungsimpulse schaffen, aber nicht leicht die Kruste durchbrechen und zu Oberflächenvulkanismus leiten.

In der ursprünglichen Zone der Magmaspaltung ist jedoch die Kruste durch das Abgleiten der Sedimentpakete und das Auseinanderweichen der Krustenteile verdünnt und gereckt. Im inneren Undationsbogen sind deshalb die Bedingungen günstig für das Aufsteigen von Magma zur Oberfläche. Dieser innere Bogen wird durch vulkanische Aktivität charakterisiert sein.

Falls die Umstände dafür günstig sind, werden die Decken wiederum vom äusserem, nichtvulkanischen Bogen in dessen Vortiefe abgleiten. Dann wird dieser äussere Bogen den Charakter des vulkanischen inneren Bogens annehmen, und durch das Einsetzen magmatischer Differentiation der Druckentlastung zufolge) wird unter dessen Vortiefe ein neuer, nichtvulkanischer, äusserer Bogen entstehen. Durch die Mächtigkeitsabnahme der Salsimaschicht unter dem ursprünglichen vulkanischen inneren Bogen wird hier (der fortgesetzten Zerlegung zufolge) der Hebungsimpuls schwächer. Im Allgemeinen wird das zentrale Gebiet, von welchem aus sich der nichtvulkanische und der vulkanische Bogen ausbreiten, den Charakter eines schwach vulkanischen Beckens zeigen; die stärkste vulkanische Aktivität herrscht an der konkaven Seite des äusseren Bogens.

Die Höhen des inneren und des äusseren Bogens werden bedingt vom Stadium der hydrostatischen Ausgleichsbewegungen, in welchen sie sich befinden und beide sind in dieser Hinsicht *unabhängig* von einander. Im westlichen Teil des Sundabogens z.B. ist der nichtvulkanische innere Bogen höher als der vulkanische äussere Bogen, im östlichen Teil dagegen ist es umgekehrt.

Der verschiedene Grad hydrostatischer Gleichgewichtserneuerung, Faktor 6, macht, dass einige Formen des Erdreliefs Dauerhaftigkeit, andere keine solche aufweisen. Die innere Reibung des Krustenmateriales und sein sehr geringer, aber endlicher Widerstand gegen Deformation in der Fliesszone verhindert, dass die Kontinente zu Kugelschalen von gleichmässiger Dicke über der schwereren Unterschicht zerfliessen (Permanenz der Kontinente). Die Hochgebirge und Tiefseegräben verursachen jedoch Spannungen in der Erdkruste, die grösser sind als der Widerstand der Gesteine, so dass diese Reliefformen infolge der hydrostatischen Ausgleichsbewegungen auf die Dauer wieder zerfliessen.

Aus obigen Darlegungen folgt, dass diese theoretische Erklärung der Entstehung der Undationen Perspektiven öffnet für die Erklärung zahl-

reicher geologischen und geophysischen empirischen Gesetzmässigkeiten. Es ist darum möglich, dass der hier eingeschlagene Weg zur Erhellung unseres Einblicks in die Entwicklungsgeschichte der Erdkruste beitragen kann.

Bandoeng, Februar, 1932.

Anthropology. — *The Anthropology of Mesopotamia and Persia* [1]). C. *The Anthropology of Persia.* By Dr. HARALD KRISCHNER and Mrs. M. KRISCHNER. (American University of Beirut.) (Communicated by Prof. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of April 2, 1932.)

Our study of the anthropology of Persia is based upon the measurements of 1140 Persians; 838 males and 302 females.

In addition we measured 98 Armenians (55 males and 43 females) from North Persia and 245 Armenians (180 males and 65 females) from New-Julfa and Isphahan. As, however, these Armenians are discussed in our preceding papers, where we also dealt with some Persian Jews and Kurds, we shall discuss here only the 1140 "Persians".

As the population in the various parts of Persia differs a good deal, we shall divide our material in three parts, those from the North of Persia, including Kermanshah, Kum and Kaschan, to a line corresponding with the 34th parallel, those from Middle-Persia, Isphahan chiefly, including the Zoroastrians from Yazd [2]), and those from South Persia (Shiraz, Bushir, Kirman). Also between the central and more Western districts anthropological differences occur — especially in the South — as will be discussed below, in speaking of the people from Yazd and Abadeh.

The curve of our 318 North-Persian males (fig. 1) as well as the curve of our 168 females (fig. 2) shows three distinct peaks. These peaks are most circumscript with the females where they occur at 74, 79 and 83, thus corresponding nearly exactly with the curve given by KAPPERS [3]), referring to 165 Persians (males and females) most of whom were also Northern Persians, in which curve the peaks occurred at 74, 78 and 83. With our males the same peaks occur as with our females, the only difference being that the 74 and 79 peaks are broader, less circumscript, the 74 peak extending also over 73 and 75 and the 79 peak extending also over 78 and 80. As however the extension in each case just covers one lower and one higher index figure, the average of these peaks remains 74 and 79 also in men.

[1]) For the two preceding papers see the same volume of these Proceedings.

[2]) Although most of our Zoroastrians were measured elsewhere, practically all of them originated from Yazd.

[3]) Contributions to the Anthropology of the Near-East, N^{0}. V Kurds, Circassians and Persians. These Proceedings Vol. 34, 1931, p. 531.

In order to understand these peaks we may refer to the analysis made by KAPPERS, who pointed out that the 83 peak among the Northern Persian is to be considered as caused by Caucasian influence. Especially in the Western Caucasus subbrachycephalic indices (81—83.9) are very frequent, as already stated by VON ERCKERT [1]) and DJAWACHISWILI [2]). The

Fig. 1. Curve of the indices of 318 males from North Persia.

Caucasian, consequently more Northern origin of our 83 index Persians is confirmed by the fact that with our Middle Persians from Isphahan (fig. 4 and 5) this peak practically disappears.

The second peak with our North-Persian women is at 79, with our

[1]) In the Eastern Caucasus, the average index of the population is higher (about 85). C.f. VON ERCKERT Kopfmessungen Kaukasischer Völker. Arch. f. Anthropologie. Bnd. 18, 1890 (p. 263 and 297) and Ibidem Bnd. 19, 1891 (p. 55, 211, 331).

[2]) DJAWACHISWILI, Die Rassenzusammensetzung der Kaukasusvölker, Ibidem, Bnd. 20, 1925, p. 77.

North-Persian men at 78—80. As the Kurdish peak is most prominent at 78—78.9, according to CHANTRE's [1]) as well as KAPPERS' researches, it is very likely that the 78—80 (resp. 79) peak in our North Persian curve represents a people of an analogous origin as the Kurds, although they did not call themselves Kurds.

There are many reasons to suggest that the race of which also the majority of the present Kurds is a branch, has a great many, widely spread branches and has practically infiltrated the whole of Persia. This appears from the fact that, whereas the 83 peak disappears with our Middle

Fig. 2. Curve of the indices of 168 females from North Persia.

Persians, the 78 top is the most outstanding one even at Isphahan, with the males as well as with the females [2]) (c.f. fig. 4 and 5).

According to SPEISER [3]) the Kurds descend from the ancient Guti or Qurṭi, who by this author are supposed to be a branch of the brachycephalic

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1) E. CHANTRE Recherches anthropologiques en Asie occidentale Arch. du Museum d'hist. naturelle de Lyon. Tome IV, 1895.

2) As long as there is no direct evidence against it we are inclined to accept that the 78 peak with the Isphahan females indicates the same race as the corresponding peak with the Isphahan males does. This is not necessarily so as very often, with dolicho- and mesocephalic races especially (c.f. the Samaritans and Phoenicians), the female index is higher than the male, the difference being even sometimes more than two.

3) E. SPEISER. Mesopotamian origins, the basic population of the Near-East. Pennsylvania and Oxford University Press, 1930.

Ponto-Zagrian stock. Whether or not this is true, this much is sure that nowadays the brachycephalic stock among the Kurds is superseded by a mesocephalic one, widely spread through the whole of Northern and Middle-Persia.

It may be that among the less ancient representatives of this mesocephalic race were the Medians of the classic Persian period. If the Median capital Ecbatana, the ruins of which are still to be seen near Hamadan, approximately indicated the centre of the Median territory this would suggest that it extended as well in our Northern as in our Middle-Persian region.

We may add to this that, if we make a curve of the indices of the 140 Aderbeidjani (112 males and 18 females) from Northern Persia, measured by CHANTRE (fig. 3) this curve also shows a high 77—78.9 peak and a small Caucasian subbrachycephalic (81) peak.

This makes it probable that also the Aderbeidjani belong to the same mesocephalic race mixed with Caucasian subbrachycephalics, exogamy, i.e.

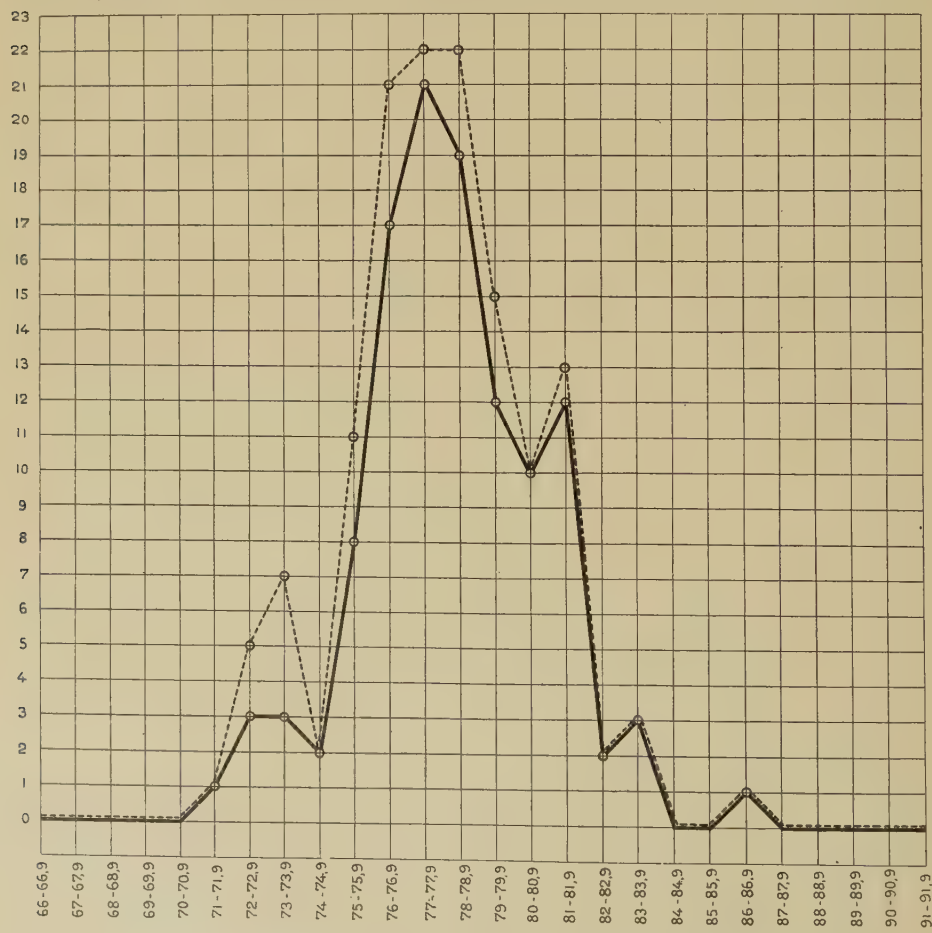

Fig. 3. Curve of the indices of 112 male Aderheidjane (continuous line) and 18 females (dotted line), measured by CHANTRE.

marriages with foreign, in casu Georgian and Circassian women being frequently found in this region, in recent times (DUNLOP [1])) as well as in ancient times (ZABOROWSKY [2])).

As the Medians were most numerous on the plateau of Iran, the whole 78—79 group might be indicated anthropologically as the *Iranians,* who thus include the majority of the Kurds, the Aderbeidjani and the 78—78.9 index Persians (cf. also DJAWACHISWILI l.c.).

Iranian indices also prevail among the 41 Tadjiks registered by CHANTRE, though brachycephalics are not rare with them (c.f. ZABOROWSKY, l.c. p. 92). Another group belonging to this category may be the Hadjemis measured by CHANTRE, who also with them found an average index of 78. They live south of Teheran.

Probably this mesocephalic Iranian race came from the North in an early period (c.f. HÜSING, l.c. and UJFALVY [3])). — Possibly the ancient Sakes in Transcaspia and the Scythians, North of the Black Sea, belonged to the same group. It is at least a striking fact that with the skulls found in Scythian kurgans (mounds) the corresponding indices frequently occur. So the average of 23 Scythian kurgan skulls described by TALKO HRYNCEVICZ [4]) had an average of 77.3 (which corresponds with about 78.3 on the head) and five male Scythian skulls from Bessarabia, described by A. DONICI [5]) had the indices: 74.3; 76.5; 77.8; 78.4 and 80.1, the average of which (77.4) corresponds with the prevailing head index of the Iranians proper, as does the average of the four skulls of Cucuteni (78) in Moldavia described by PITTARD [6]).

As the Scythian kurgan people is supposed to have influenced the prehellenic Pelasgic and consequently also the hellenic population of Greece (MYRES [7])) and as a similar index still occurs in Crete (HAWES [8]), VON LUSCHAN [9]), Greece and Anatolia [10]), the spread of these mesophalic Iranians, closely related to the Nordic type [11]), apparently was an extensive one, already in ancient times.

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1) DUNLOP, Perzië voorheen en thans.

2) ZABOROWSKY. Les peuples Aryens d'Asie et d'Europe, Doin, Paris, 1908, p. 167.

3) UJFALVY. Les peuples Aryens au Nord et au Sud de l'Indou-Kouch 1896 (quoted from Ripley The peoples of Europe).

4) TALKO HRYNCEVICZ. Contribution à l'étude des Kourganes de l'Ukraine, Krakow, 1900. Polish, quoted from DONICI.

5) DONICI. Notes sur quelques crânes scythes. Revue anthropologique 40ième année N°. 7—9, 1930, p. 233, and A. DONICI, Contribution à l'étude anthropologique des Scythes; Archives suisses d'Anthropologie générale. Tome V, N°. 3, 1930—31, p. 321; In this paper DONICI gives the indices of 7 male skulls as being 75, 5; 77; 77, 1; 79, 2; 80, 4 and 87; of two female skulls as being 81, 5 and 86, 98.

6) E. PITTARD, Ossements humains provenant de la station de Cucuteni. Bulletin de la Société des Sciences de Bucarest, 1904.

7) MYRES. Who were the Greeks? Calif. University Press, 1930.

8) HAWES. Report on Crete for the Brit. Assoc. f. the adv. of science 1903 and 1912.

9) VON LUSCHAN. Beiträge zur Anthropologie von Kreta. Zeitschr. f. Ethnol. B. 45, 1913, p. 307.

10 ARIËNS KAPPERS. Contributions to the Anthropology of the Near-East VI. Turks and Greeks. Proc. of the Kon. Akad. v. Wetensch. Amsterdam, Vol. 34, 1931.

11) That the Kurgan people extended far North appears as well from a paper by Count BOBRINSKY: Kourganes et trouvailles archéologiques accidentelles près Smiéla, gouv. de Kieff, Saint Petersburg 1887; as from the findings by BOGDANOFF near Pola and Moscou (c.f. BOGDANOFF. Crânes provenant des Kourganes près Pola. Bulletin de

It is a curious fact that while the male skulls found in the kurgans are distinctly mesocephalic, in the kurgans examined by DONICI three female skulls were found and all three were either brachycephalic or hyperbrachycephalic, which may indicate that already at that early period the brachycephalic Caucasian and Armenoid races mixed with this people by marriage. Considering the dominant character of brachycephaly it is interesting to note that the ancient mesocephalic population of Southern and Middle-Russia is now superseded by a population which is prevailing brachycephalic (index 84) as are the Balkan Slavs [1]). This present population of Russia probably is closely related to the Caucasian brachycephalics [2]).

These Northern mesocephalic Iranians [3]) should be well distinguished from the dolichocephalic Indo-Persian race (among which the ancient "Persians s. str.") to which we now proceed.

Returning to our Northern Persian curves in fig. 1 and 2 we see that the third peak with the males and especially with the females is at 74 (males 73—75), as also found by KAPPERS.

This peak is again of great anthropological and historical interest as it is the most outstanding one with the Zoroastrians (fig. 6).

Hitherto there are very few data concerning the Persian Zoroastrians or Guebers. The only one who paid more attention to their anthropological characteristics was DE KHANIKOFF [4]), who examined some Zoroastrians at Yazd and found them to be dolichocephalic, DE KHANIKOFF also sent five Zoroastrian skulls (3 from Yazd, 2 from Kirman) to the Museum of Natural History in St. Petersburg, where they were examined by VON BAER, who stated that they resembled the Hindou type (these skulls had an average index of 70, corresponding with a head index of about 71.5).

As only few descendants of the ancient Perses stuck to the Zoroastrian religion, most of them being compelled either to accept Mohammedanism or to flee to India (see below), it is not strange that the same racial characteristic nowadays occurs frequently with non Zoroastrian inhabitants of Persia.

But the index 74 has a still greater importance. The ancient Persians themselves probably were only a part of a more widely spread race — extending from Caucasia and Transcaspia to India. So one might

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la Socciété des amis des Sciences natur., anthrop. et ethnogr. de Moscou 1878; The same. Materiaux pour l'anthropologie de la période des Kourganes dans le gouvernement de Moscou. Ibidem 1867 and The same. Quelle est la race la plus ancienne de la Russie? Ibidem 1892. (Russian, quoted from DONICI).

[1]) RIPLEY. Peoples of Europe, and CWIRKO-GODYCKI. Les Slaves méridionaux. Revue anthropologique, 40ième Année, 1930.

[2]) We do not of course infer that the brachycephalic Russian Slavs originate from the Caucasus, but only that there probably is a racial kinship between them, perhaps a common origin.

[3]) This race may correspond to HADDON's Irano-mediterreanean race. See our discussion on the last page.

[4]) DE KHANIKOFF. Mémoire sur l'Ethnografie de la Perse, Martinet, Paris, 1866.

distinguish this race from the Iranians by calling it the Indo-Persian race [1]). Also the work of HÜSING [2]) on the various Aryan languages, in ancient Persia may be quoted in favor of the fundamental distinction between our Iranians proper and the Indo-Persian group.

The occurrence of this dolicho-cephalic people in North-Persia in addition to the mesocephalics and subbrachycephalic Caucasians has been emphasized also by KAPPERS.

Whatever may be the truth about the extension of the dolichocephalic Indo-Persian and mesocephalic Iranian race in the ancient times in the Near-East and in the Aegaean, it is a striking fact that the skulls found in and near Troy, described by R. VIRCHOW, were prevailing dolichocephalic, not mesocephalic. Hitherto only few mesocephalic skulls are found on the west coast of Anatolia, dating from such an ancient period, but at GEZER both occurred [3]).

Curiously at Isphahan the 74 index is not striking but here next the 78 peak, not failing even among the Zoroastrians (see fig. 6) a 75 peak occurs. Whether or not this peak is due to a group analogous to the above mentioned dolichocephalics is not sure, but possible, considering the fact that in the North the 74 and 75 peaks are equally high and together are separated from the rest.

If this is true a part of the population of Middle-Persia would be related to the ancient Perses [1]) and another part to the Iranians (c.f. fig. 4 and 5).

We may not omit calling attention to the smaller peaks occurring at 72 in the male Isphahan curve (73 in the female).

Such indices, and even lower ones, become more frequent proceeding South-East. Considering the fact that in the South-Eastern districts (Yazd fig. 6, Abadeh, fig. 7), somewhat lower dolichocephalic indices prevail, as also occurs in Balouschistan and part of India, the most probable explanation is that we have to consider this as a Hindou influence, the index with the Hindou population (also with the majority of the Afghans?) being usually dolichocephalic. This may also explain that, although the majority of our Zoroastrians have an index of 74, also with them lower indices are not so rare.

Further South near Shiraz and on the Persian gulf the relations are different. Here (fig. 8) the Hindou influence considerably decreases as appears from the curve of our measurements in this part of Persia compared

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[1]). This race may correspond to HADDON's Indo Afghan type, although more researches on the anthropology of Afghanistan are necessary to verify this assertion. C.f. HADDON's classification in his Races of man, Cambridge Univ. Press, 1924, p. 86 a. f.

[2]) HÜSING. Völkerschichten in Iran. Mitt. der Anthr. Ges. in Wien, Bnd. 44, 1916, p. 199. C.f. also UNGNAD. Die ältesten Völkerwanderungen Vorderasiëns, 1923.

[3]) MACALISTER's curve of the indices of Presemitic skulls, found at GEZER, shows a peak at 73 and one at 78. Cf. Excavations at GEZER, London, 1912.

[4]) It is a wellknown fact that with the decline of the Sassanide empire the ancient Perses (or Parsi) fled to India. Curiously these Indian Parsis are said to be subbrachycephalic, according to DENIKER (Peuples en Races de la Terre, Paris, 1900, p. 672) and VON LUSCHAN Völker, Rassen und Sprachen, Berlin, 1920, p. 111.

to the results obtained in more Eastern districts as Yazd and Abadeh (c.f. fig. 6 and 7).

Although lower indices like 73 are not failing in South-West Persia they stand in the minority as compared to the mesocephalic and sub-

Fig. 4. Curve of the indices of 209 male Persians from Isphahan.

brachycephalic indices, — the 77 and 83 peaks being by far the prevailing ones in this region, especially the 77—77.9 peak.

Although similar peaks occur with the Northern Persians, and there are to be explained as Iranian and Caucasian peaks, a direct Caucasian, influence so far South is not probable, subbrachycephalic Caucasian indices being rare already at Isphahan. Besides the Iranian mesocephalics have usually a slightly higher index than 77 (varying between 78

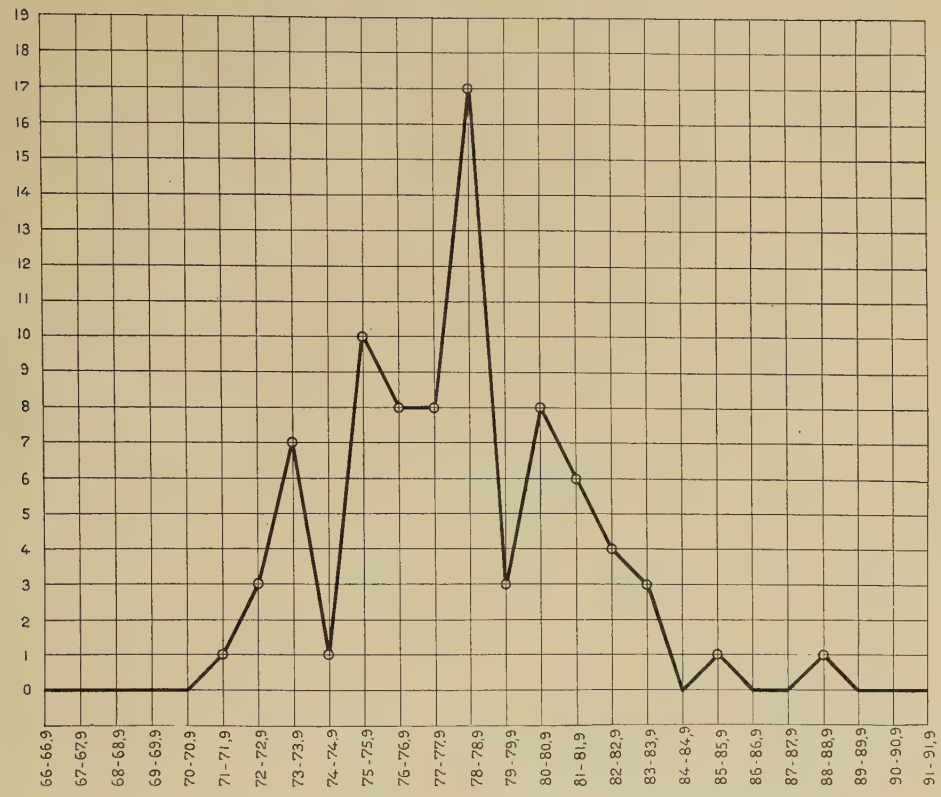

Fig. 5. Curve of the indices of 82 female Persians from Isphahan.

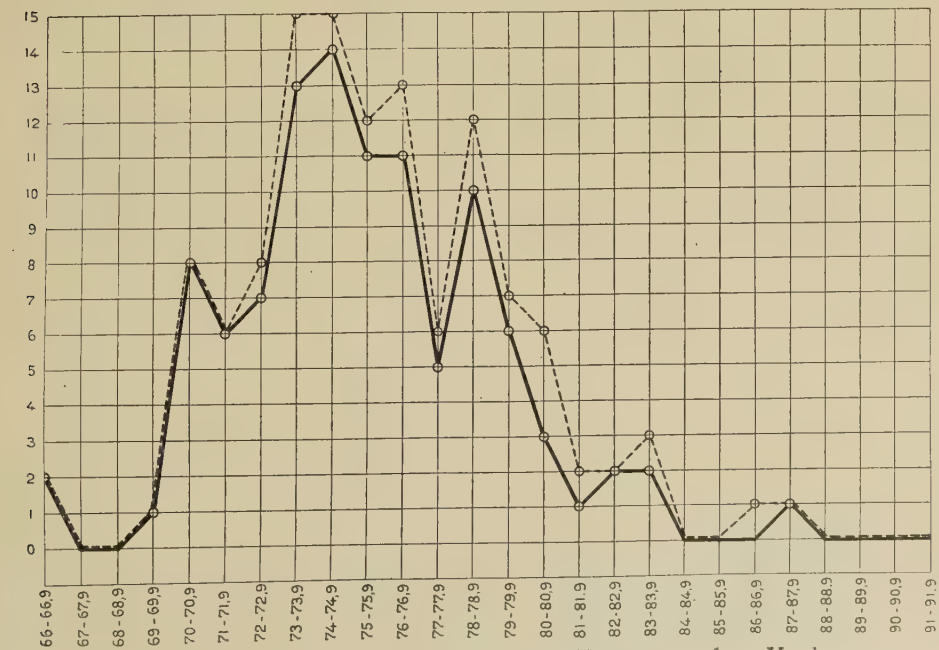

Fig. 6. Curve of the indices of 103 male Zoroastrians from Yazd (continuous line) and 16 females (dotted line).

and 79). As Shiraz lies near the province Arabistan it does not seem impossible that the great frequency of these two indices, so typical of the

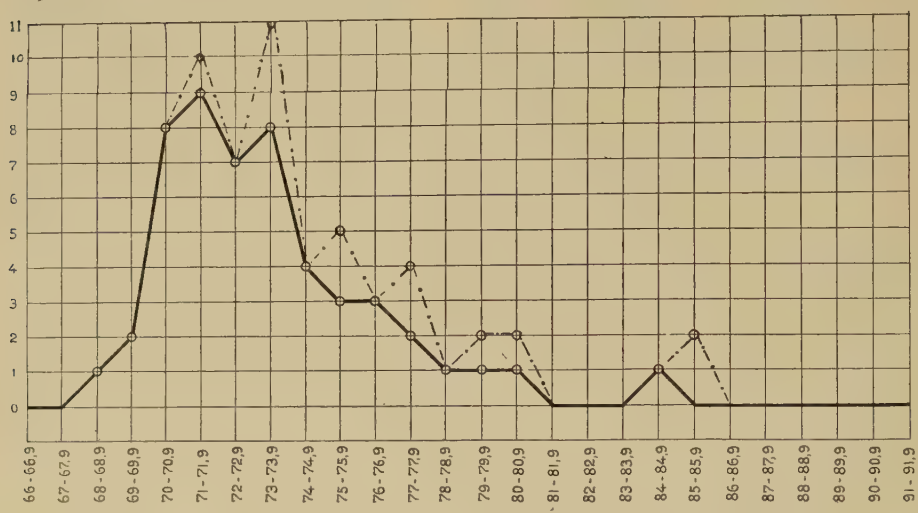

Fig. 7. Curve of the indices of 51 males from Abadah (continuous line) and 12 females (dotted line).

Adnan (77 index) and Kokhtan Arabs (83 index) are due to Arabic influence.

In connection herewith it should be emphasised that whereas Upper-Mesopotamia is separated from North- and Middle-Persia by mountainous ranges, Lower Mesopotamia continues smoothly into South-West Persia, which, moreover, is anthropologically connected with Arabia proper by the Persian gulf, water being the best means of intercourse and racial exchange, especially in ancient times.

Similarly as in Sumerian times the culture of Southern Persia influenced Lower Mesopotamia (FRANKFORT [1]), so vice-versa the two Arab types of Mesopotamia may have followed the propagation of the Islam into Southern Persia. Indeed many facts may be quoted to prove that between Lower Mesopotamia and Southern Persia a vivid intercourse existed both ways, culturally as well as anthropologically, Arabic influence on Persia being especially strong since the caliphate of Baghdad.

This would also explain that more centrally, at Yazd and Abadeh, those Arabic indices disappear and the lower Indo-Persian indices prevail.

Finally a few words concerning the *Bakhtyari* of whom hitherto so few measurements have been published. Also our data about this mountainous people only concern three males, one of whom was mesocephalic [2]) (78.4),

[1]) See the interesting address by Dr. H. FRANKFORT at the International congress of Orientalists, Leiden, 1931.

[2]) According to DUHOUSSET (quoted by KHANIKOFF) mesocephalic indices prevail with the present Lori, the next neighbours of the Bakhtyari, frequently mixed with them. SPEISER, however, considers the Lori or at least the ancient Lullu, from whom they derive their name as being also a part of his brachycephalic Ponto-Zagrian stock.

while the two others were extremely brachycephalic: 91 and 93.4. Probably the latter represent the true Bakhtyari characteristic, as it agrees

Fig. 8. Curve of the indices of 153 males from South-West Persia (continuous line) and and 23 females (dotted line).

with the figures found by GAUTIER (quoted by CHANTRE) who measured nine Bakhtyari with an average index of 89.32.

Such high indices are also frequently found in the Lebanon, especially with the Druses and, as according to LAYARD [1]) the Bakhtyari may come from Syria, whence they migrated, according to DE KHANIKOFF (l.c. supra)

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[1]) In LAYARD's Description of the Province of Chusistan (Journ. of the Roy. Geogr. Society, 1846, p. 7) it is stated that according to the tradition of the Bakhtyari themselves they originate from Es Shams (the Arabic name of Damascus). If this be true their brachycephalic index may be explained by a racial relation with the Lebanese and with the Druses of the Hauran (immediately South to Damascus).

after the 13th century A. D., it is possible that there exists a racial relationship between both groups.

Conclusion.

Concluding we may say that — apart from special groups, as the Armenians and Jews, which we discussed in a preceding paper — the population of Persia consists of two groups or races chiefly.

The most numerous is the mesocephalic 78—79 index race, which we propose to call the "Iranians proper". To this group also most of the present Kurds, Aderbeidjani, Tadjiks and Hadjemis belong, but its spread goes far beyond these special groups. They are very numerous in Northern and Middle Persia.

Second to this is the dolichocephalic Indo-Persian race, which — although not failing in North and Middle Persia — is more numerous in the South-Eastern districts. They are a dolichocephalic 73—75 race, mixed with Hindou infiltrations.

The Iranians may represent the Medes of the ancient times, whereas the Indo-Persians (which include the Zoroastrians or Guebers) are remnants of the ancient Perses.

In addition to these two races there is a strong subbrachycephalic Caucasian infiltration in North-Persia and an Adnan and Kokhtan Arab infiltration in the South Western part of Persia, especially near the Persian Gulf.

We finally have to consider the question if there may be an anthropological connection between the Iranian race, as defined in this paper, and the Adnan Arabs, as seems to be involved in the name "Irano-mediterraneans" used by HADDON (l.c. supra).

Although the prevailing cephalic index in both groups does not differ very much and the prevailing of the Adnan Arabs in the Northern part chiefly of the Syrian desert, coincides with the chief latitude of spread of the Iranians in Persia, more researches would be necessary for such a statement.

That the linguistic difference — one group speaking a Semitic, the other a Caucasian or Aryan language — is no sufficient reason against such an anthropological relation, may result from our previous papers in these Proceedings, — where we also quoted Sir ARTHUR KEITHs opinion on this subject. This question evidently is paralel to the often discussed relation between the mesocephalic Nordics and Mediterraneans.

Anatomy. — *Considerations on Brainmechanics on account of a peculiar asymmetry in two human brains.* By Dr. A. J. VAN BORK—FELTKAMP. (Communicated by Prof. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of April 2, 1932.)

To get a general idea on the phylogeny of the fissuration in the parieto-occipital region of the primate brain one may start with the condition in Ateles (ARIËNS KAPPERS, 1921), which is principally characterised by the presence of a lunate sulcus with a short s. praelunatus, and of a transverse occipital fissure as terminal bifurcation of the intraparietal.

In the katarrhine apes the lunate and the transverse occipital fissure can no longer be distinguished as separate fissures, since the predominating development of the occipital region causes the caudal lip of the lunate to form an operculum which growing frontally overlaps the cortex in front of it including the region in which the transverse occipital fissure occurs.

In the human brain, however, in this same region a new development of the peri- and parastriate areae (18 and 19 of BRODMANN) causes the anterior wall of the fossa simiarum to protrude to the surface which consequently shows again some resemblance to Ateles. We owe this deduction of the homologies to the publications of ZUCKERKANDL and especially of ELLIOT SMITH, that finished many controversies.

The first cerebrum the parieto-occipital region of which I am going to describe is one of the Chinese brains presented by Prof. J. L. SHELLSHEAR in Hongkong to Prof. J. P. KLEIWEG DE ZWAAN for the Royal Colonial Institute at Amsterdam.

A reproduction of the mesial side (fig. 1) shows that this brain — such as more are to be found among those from Hongkong (17 out of 49; VAN BORK 1930) — bears a striking resemblance to the brain of the Northern Chinese, especially by the oblique course of the ramus ascendens of the calloso-marginal fissure (10), the great general height — and callosum index (0.558 and 0.367 respectively), the hook-shaped splenium of the callosum, the pointed outline of the frontal pole, the small stem-angle (97.75°), and the small parieto-occipital angle (37.25°) [1]. It has appeared from the figures of KAPPERS (1930), that this angle, which is formed by the basal callosum line and the main direction of the parieto-occipital fissure is larger for hyperbrachencephalic Armenian and other hyperbrachencephalic brains and smaller for dolenchocephalic brains. If, however, we have to do with a relatively short cerebrum, the smaller length of which is compensated for not so much in width as in height, as is the rather meso- or subbrachencephalic Northern-

[1]) These measurements are taken in the left hemisphere, not in the right hemisphere reproduced in fig. 1.

Chinese, the parieto-occipital angle becomes smaller, owing to the splenium taking a higher position, the consequence of which is, that the basal callosum line topples forwards with

Fig. 1

regard to the stem axis. As a result of this the stem-angle becomes also smaller (c.f. also KAPPERS 1926, 1929).

Fig. 2 reveals a peculiar asymmetry in the fissuration of the praeoccipital region. On both sides a well developed s. lunatus (18) is to be found in front of which there is on the left a sulcus 17, the terminal bifurcation of the intraparietal (16). This bifurcation forms the transverse occipital fissure. On the right, however, 16 is merged into 18, while 17 is hardly visible; so here the so much larger occipital operculum overlaps a part of the cortex, which on the left side lies on the surface. On the same side the s. paramesialis of ELL. SMITH (22) has likewise got detached from the lunate (18). Besides 22 is much longer on the left than on the right as a consequence of the larger extent of the cortex on the surface. [1])

The cortex caudal to 18, the area striata, in both hemispheres shows the sulci characteristic of this region, viz. a s. ypsiliformis (19) and a f. calcarina (20). On the right the calcarine is exceedingly short (fig. 1), whereas on the left the fissure continues some way on the convexity (fig. 2). I shall deal again with this point after having discussed the

[1]) In this respect it is characterictic that in phylogeny the inferior occipital fissure, which lies behind 18 gets prolonged first, and only after this the s. praelunatus (18p), which lies in front of it.

second cerebrum. So far as concerns the first, I should prefer to draw the attention to the different character of the fissuration on the left and

Fig. 2

on the right in the praeoccipital region. A few explanatory comments should first be made.

In the literature of half a century ago, when the study of the sulci and gyri was still in its initial stage, mention was already made of some connection between the course of the sulci and the shape of the cerebra. (CALORI, 1870; MEYER, 1876; RÜDINGER, 1877; ZUCKERKANDL, 1883). It appears that upon the whole the longitudinal fissuration predominates in a longer cerebrum, and in a shorter the transverse, as I could confirm on account of a comparison of Chinese and Dutch brains (1930). Confining ourselves to the temporal lobe which in itself is an elongated part of the brain, the longitudinal course of the four sulci occurring on it (superior and inferior temporal, occipito-temporal and collateral sulci) indicates that the correlation demonstrated by the above mentioned authors as for the whole brain, also applies to parts of it. A comparison of the two hemispheres of fig. 2 also points to this: in consequence of the emergence of the transverse occipital fissure on the left the region in front of the lunate sulcus increases in frontocaudal dimension. This increase in fronto-caudal dimension of the left praeoccipital lobe appears to influence the direction of the sulci occurring on it: on the right the branches of the parieto-occipital sulcus (21) continuing on the convexity have a predominating transverse course; on the left, on the other hand

they are considerably elongated in frontocaudal direction, while here the transverse branche of 16, (×), inserted on the right between the legs of 21 is lacking. The terminal bifurcation of the lunate, a part of which forms the praelunate sulcus (18p), has a nearly transverse position on the right, on the left, however, it runs about parallel with the tentorial edge, and consequently has a longitudinal course. Likewise the influence of the shape of the region in which the sulcus is situated is noticeable from the direction of the angular sulcus (25) and the anterior occipital (26), that may be considered as branches of the superior temporal. (WANG and KAPPERS, 1924; SHELLSHEAR, 1926): on the right they have a transverse course, on the left a rather longitudinal one.

This difference between left and right is all the more significant, because it appears from this that a change in the shape of a region may result in causing the sulci to deviate from their characteristic direction: so the bifurcation of 21 belongs to the transverse fissuration [1]), similarly the sulci 25 and 26. On the other hand 18p forms part of the longitudinal system, and in our case is allowed to take its typical direction therefore only on the left. The asymmetry of the four sulci described thus shows still further consequences of the form (c.f. fig. 2) than implied in the opinion advanced by the above mentioned authors.

Fig. 3A, the second brain, shows the same asymmetry in development as mentioned above. This Dutch female cerebrum formed part of a collection which was presented to the Institute for Brain research by Dr. E. HAMMER.

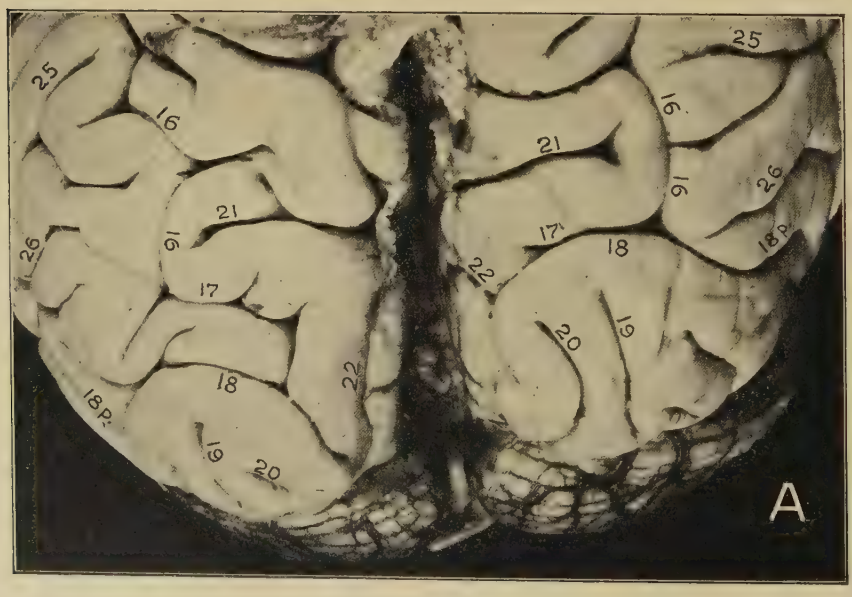

Fig. 3A

[1]) These branches have been described as component parts of the parieto-occipital by ELL. SMITH (1904).

Apart from the great resemblance to the cerebrum discussed above, there is an important difference: whereas there was a great asymmetry in the direction of fissuration in the praeoccipital region in the first brain explained by a widening on the left side as compared to the right, in this second case the asymmetry is very marked on the mesial side.

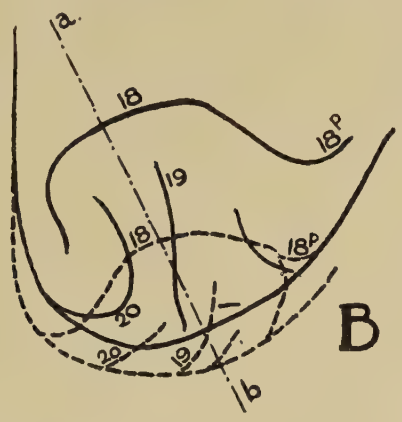

Fig. 3B

On the convexity (fig. 3A) it is confined to the development on the left of the terminal bifurcation of 21, which is hardly visible on the right, and to an asymmetry of the paramesial (22), which is of exactly the same kind as in the cerebrum first described.

Fig. 3C

As we know the lunate practically is the limiting sulcus of the area striata. According to Ell. Smith (1907, 1929) the cytotectonic extent of the area striata is equal in both hemispheres, no matter how much the shape and the folds on the left and the right may differ (c.f. also Von Economo 1930). As to its smaller extent on the left convexity the area striata aims at compensation, as is especially apparent in the calcarine (20) of fig. 3C. Of this fissure the part situated in front of the confluence with 21 is the limiting sulcus of the area striata, but the remaining part, which is much longer, is situated entirely in region 17.

so here both walls contribute to its extension. Consequently it appears from the hooklike calcarine in fig. 3C that the pars intrastriata of the calcarine is considerably larger on the left than on the right, through which the difference in surface of region 17 on the convexity is compensated for.

This hook in the calcarine and the location of the fissure somewhat remote from the tentorial edge is more or less characteristic for the Northern-Chinese brain (the hook occurring in 46.2 per cent of the cases against 18.4 per cent in the Dutch) [1]; on the other hand it appeared that in 60 reproductions of hemisphere of Esthonians (LANDAU, 1910) this hook occurred only three times, so I consider it to be a valuable anthropological characteristic. Our second brain gives an additional indication in the same direction. In fig. 3B the reflected image of the left occipital pole has been drawn in dotted lines across that of the right one; the line a—b indicates how the operculum on the left has shifted with regard to the right. As this line intersects the outline of the cerebrum perpendicularly, it at the same time indicates the direction of the replacement of the medial surface. The direction of this replacement, which in this especial case occurs in consequence of the asymmetry in the development, corresponds exactly to the division of the cerebral mass in the Northern-Chinese brain, which compared with other races is rather short, which shortness is compensated for by height (tendency to hypsencephaly). The hook in the calcarine rather characteristic of the Chinese is consequently more than a chance capriciousness of the sulcus-pattern, but a feature correlated with the general shape. As usually it does not modify the aspect of a single fold, but of the folding in general: also in this case the sulci situated below and above 20 show the influence of the replacement.

The hook in the calcarine is rather sharp, and in my opinion we should assume that it is caused not so much by the tendency of a cortex field to increase, but mechanically by the relative shortness of the brain. This also appears from the relation of the calcar avis, the eminentia collateralis and the bulbus cornu posterioris. Externally the hook in the calcarine in Northern-Chinese is often still emphasized by the occurrence of a "basal transverse fissure" in the concavity of the calcarine.

My starting-point was consequently formed by two brains, which show the same asymmetry, and yet display distinct differences in the accompanying phenomena, which, however, can be accounted for in each of these cases by the special form of the asymmetry. Of course the question immediately arises why in the first case the relaxation of a certain part of the brain and in the second the pressure in another part predominates. Probably the brain-indices may give an indication. The index of the first

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[1]) The location is rather remote from the tentorial edge in the Chinese in 96.2 %, in the Dutch in 78.3 %.

cerebrum is 75.43, of the second 86.3. It moreover appears that in the brain with the lower index the lunate itself from being more transverse becomes somewhat longitudinal in its replacement to the pole; the brachencephalic brain on the other hand, retains the character of its more transverse fissuration also in the left praeoccipital region, although as a matter of fact the distance between 18p and 25 is much larger than on the right. In this cerebrum, however, this difference is used for creating a number of small transverse sulci (fig. 3A).

Consequently we must assume, that the asymmetrical development has modified the character of the fissuration in some parts of the brain, but in either of the cases this modification corresponds to the index, in other words the influence of the brain-index overrules that of the asymmetry treated above.

As to the compensation of the area striata of the first brain, it has already been pointed out, that on the right the calcarine (20) is exceedingly short; on the left, however, this fissure clearly extends some way over the occipital pole (fig. 1 and 2).

ELL. SMITH (1907) considers asymmetry of the occipital pole as a human characteristic, which results in asymmetry of the transverse sinus. VAN GELDEREN (1924—26) supposes that this asymmetry in the occipital lobes is the most probable cause of the *persistence* of the asymmetrical sinus which, however, as appears from his investigations already occurs in an early stage of development[1]). This asymmetry is somewhat neutralized in the ontogeny by the development of the emissaria, which neutralization is promoted by the possible development of a couple of sinus occipitales (RIJNDERS, 1929).

The greater extent of the area striata on the left convexity is accompanied by smaller capacity of the sinus transversus on that side (ELL. SMITH). This condition was found by ELL. SMITH in Egyptians in 80 per cent of the cases[2]).

Likewise LE DOUBLE (1903) describes as the most frequently occurring type of the occipital bone the type in which an impression of the right transverse sinus predominates (in 200 cases 137 times, thus in about 70 %). A rather deviating statistic is quoted by LOTH (1931) from HENRICI and KIKUCHI (1903—04), who on account of an examination of the veins themselves (35 cases), state the occurrence of a greater capacity of the right transverse sinus to be 33 per cent; in the same work SPERINO (1884) is cited who 269 times in 512 cases, thus in about 50 %, found a greater right sinus transversus. In view of so little conformity we agree with LOTH that, also from an anthropological point of view this subject may be reexamined.

In both my cases the surface of the area striata on the right convexity is considerably larger than on the left, and thus this is not in accordance with the rule mentioned by ELL. SMITH, the more so as in

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[1]) Between the 2[d] and 3[d] foetal month.

[2]) In the picture ELL. SMITH gives of this condition, the left as well as the right transverse occipital is detached from the lunate, yet the space between these fissures is in the right hemisphere considerably larger than in the left.

the first cerebrum the right transverse sinus has formed a clear impression, and in the second the right as well as the left.

EXPLANATION OF THE NUMBERS OF SULCI.

10. s. callosomarginalis.
16. s. intraparietalis.
17. s. occipitalis transversus.
18. s. lunatus.
18p. s. praelunatus.
19. s. ypsiliformis.
20. f. calcarina.
21. s. parieto-occipitalis.
22. s. paramesialis.
25. s. angularis.
26. s. occipitalis anterior.

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Aerodynamics. — *Oscillographic records of the turbulent motion developing in a boundary layer from a sheet of discontinuity.* By M. ZIEGLER. (Mededeeling N°. 23 uit het Laboratorium voor Aero- en Hydrodynamica der Technische Hoogeschool te Delft.) (Communicated by Prof. J. M. BURGERS.)

(Communicated at the meeting of April 2, 1932.)

1. With the experimental arrangement described in „Mededeeling 21" from this laboratory, a great number of records have been taken in order to investigate the development of turbulent motion in the boundary layer. [1])

The problem of turbulence and its origin has been the subject of many investigations, both experimental and theoretical. It is generally known that, as soon as the Reynolds number $R_\delta = \frac{\varrho V \delta}{\mu}$ (δ being the thickness of the boundary layer) reaches a critical value, which depends to a certain degree on the magnitude of exterior disturbances, laminar motion becomes unstable and gives way to turbulence.

A very convenient object for experimenting is the boundary layer along a flat smooth plate. Such a boundary layer has been investigated by VAN DER HEGGE ZIJNEN, who measured at a great number of points the distribution of the mean velocity along a glass plate, the leading edge of which was sharpened, and which was mounted parallel to the direction of flow. [2])

In the case which he describes, we start with a boundary layer in laminar motion, which becomes turbulent at a certain distance from the beginning of the layer. (The transition occurs for a value of R = ca. 2000.) A similar state of things could be found with our arrangement. A number of oscillographic records of the velocity fluctuations along a glass plate showed that, for a certain position of this latter, the boundary layer is steady over a certain distance, before it becomes turbulent. In the region of transition the laminar flow, at irregular intervals, is interrupted by short periods of complete turbulence. These periods grow in duration and in number as we go downstream. It may be assumed, that for this position of the plate, there do not arise perceptible disturbances at the leading edge; the stagnation point — the dividing point of the flow —, perhaps may be just on it.

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[1]) See M. ZIEGLER, these Proceedings, **34**, p. 663, 1931. A complete arrangement for the investigation, the measurement and the recording of rapid airspeed fluctuations with very thin and short hot wires.

[2]) See B. G. VAN DER HEGGE ZIJNEN, Measurements of the velocity distribution in the boundary layer along a plane surface (thesis Delft, 1924).

Another case is obtained when, owing to great initial disturbances, turbulent motion develops at once, a region of laminar flow being absent. This state of things could be obtained by slightly lifting up the leading edge of the plate — the plate originally being horizontal. Immediately behind the leading edge, measurements show the existence of a sheet of discontinuity, which must be regarded as the origin of the turbulence. Though we have no experimental data of the velocity distribution at the under side of the plate, it may be assumed that the stagnation point now has shifted to that side and that a part of the flow has to pass around the edge to the upper side — where the measurements are made —, giving rise to the formation of the sheet of discontinuity. The condition of the flow differs very much from that obtained in the first case; especially all phenomena occur within a very short space.

As during the course of the work many problems had to be looked after, and refinements of the methods of measurement had to be introduced, the investigations of the first case have not yet been finished. In this communication we shall only discuss the experimental results concerning the development of the turbulence originating from the disturbance of the leading edge. [1])

2. The general arrangement of the plate and of the measuring instruments, mounted in the smaller windchannel of the laboratory, is shown in fig. 1. The glass plate is provided with a metallic nose having a sharp

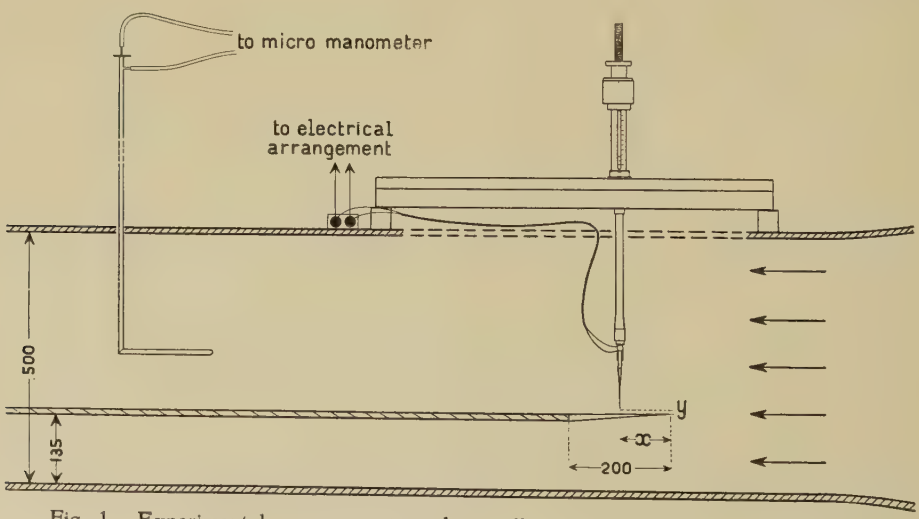


Fig. 1. Experimental arrangement in the smaller windchannel of the laboratory. (The dimensions are given in mm.)

[1]) The case may be compared to the problem of the flow at the entrance of a pipe, investigated with the aid of coloured bands in water by A. NAUMAN. Inaugural Dissertation, Leipzig 1931: Experimentelle Untersuchungen über die Entstehung der turbulenten Rohrströmung.

leading edge. This nose, which had been fixed to the plate some time ago for other measurements, is made of two sheets of zinc, fitting very closely both to the glass plate and to each other. The surface has been smoothed as good as possible but is not absolutely flat.

As all considered phenomena happen within a relatively short distance, the measurements were limited to the boundary layer along the zinc nose. At the beginning of the investigation the metal was not smoothed so carefully and the leading edge was less sharp than afterwards; the phenomena observed at that time, however, do not differ from those recorded in the later work. The condition of the flow appears to be determined by the general form of the disturbing object, and it is thus not to be expected that these phenomena will differ materially from those which would arise if the plate was absolutely flat and smooth, and the leading edge still sharper.

The platinum wires used for these experiments (diameter 0.005 mm, length ca. 1 mm, position perpendicular to the motion of the air and parallel to the plate) could be displaced in the longitudinal direction of the channel; for the motion in vertical direction a micrometer screw was provided.

The preparation of the wires has been described in the publication mentioned before. An important improvement since then is the use of Wollaston wire, the exterior diameter of which is only 0.050 mm. The thin platinum wire thus finally is mounted between two threads of $^1/_{20}$ mm diameter, having a length from 5 to 10 mm, and a rigidity just sufficient for stretching the wire. It was found that the wires were much less liable to breaking by mechanical causes; besides, the perturbation caused by the anemometer in the field of flow is still much less than by the former way of mounting.

3. In addition to oscillograph records of velocity fluctuations the mean velocity V was measured as a function of the distance from the surface of the plate, for various distances from the leading edge. The values of this mean velocity were derived from the indication of a slow galvanometer, used in the bridge, which was calibrated by bringing the wire in the free stream at a great distance from the plate and changing the air velocity in the windchannel. As the sensitivity increases considerably for low velocities, the values of the mean velocity obtained may be more or less in error at those points where the fluctuations of the velocity are great. As the only object of these measurements, however, was to obtain an approximate picture of the flow in the boundary layer, a great accuracy was not necessary.

In order to determine the position of a point of the boundary layer, the distance from the leading edge is denoted by x; the vertical displacement of the wire, as read from the micrometer screw, is denoted by y, $y = 0$ corresponding to the level of the leading edge. As the upper surface of

the nose is inclined downward in the direction of flow, the distance from this surface, to be denoted by y', is not equal to y; the differences are to be seen from fig. 3.

4. The velocity curves for 8 distances from the leading edge have been reproduced in fig. 2. From these curves a general map of the velocity distribution has been derived (see fig. 3).

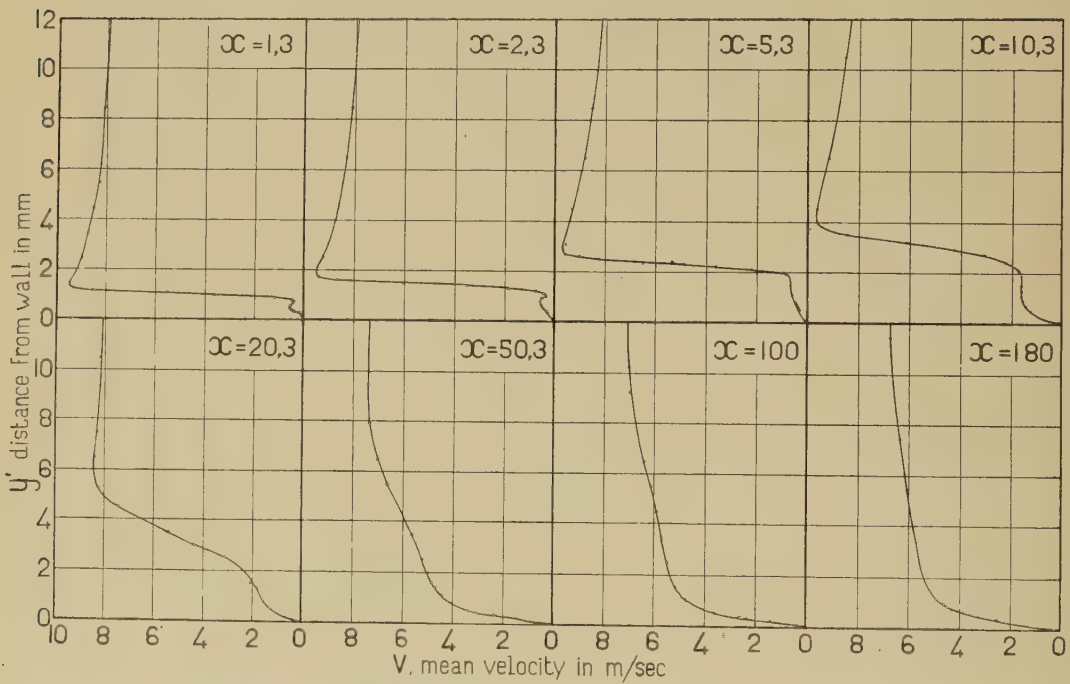


Fig. 2. Curves of the mean velocity V as a function of the distance from the surface of the plate for various distances from the leading edge.

With small values of x, the layer of discontinuity arising at the leading edge, is very marked. At $x = 1.3$ mm or 2.3 mm f.i. there is a jump in the value of V of about 9 m/sec over an interval of $\frac{1}{2}$ mm in the direction of y. As is to be expected this sharp discontinuity cannot remain unchanged over a long distance. While it is still very pronounced at $x =$ 10.3 mm, already at $x = 20.3$ mm the progress from high to low velocities is much more gradual, and at $x = 50$ mm the sinuosity has practically disappeared.

The velocity curves for $x = 1.3$ mm and $x = 2.3$ mm show a singular bend at $y =$ ca. 1 mm which seems to indicate the presence of a retrograde motion of the air at this place. In the region of low velocities under the layer of discontinuity apparently a certain amount of rotation is gathered, constituting a stationary vortex. In this region the x component of the velocity is not dominating; this makes it difficult to get a clear

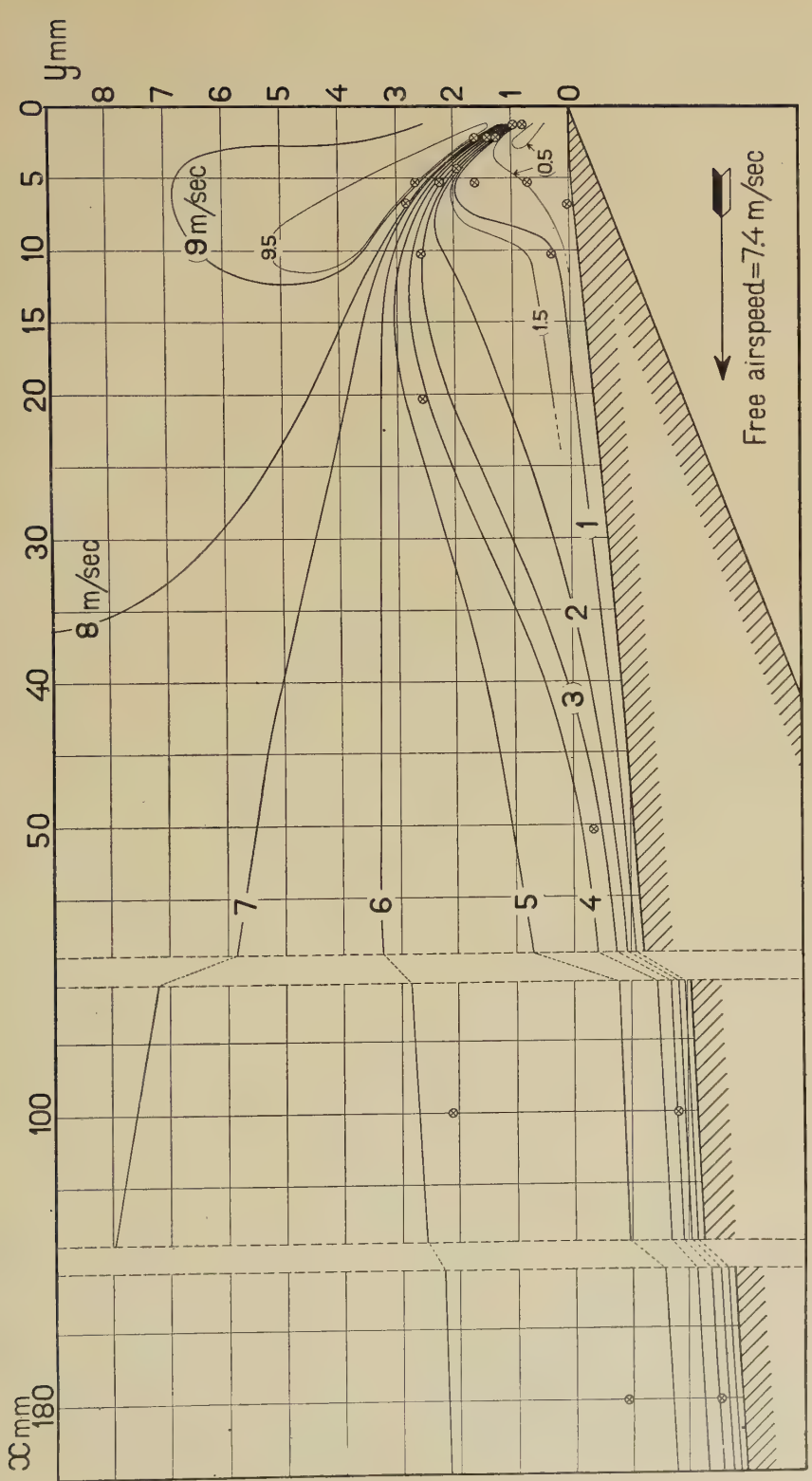


Fig. 3. General map of the velocity distribution in the neighbourhood of the nose. The little circles indicate the points of the field corresponding respectively to each oscillogram.

view of the real aspect of the field from the relatively small number of observed values, as with a single hot wire it is only possible to determine the *absolute* velocity in the x—y plane.

5. Records of the velocity fluctuations were taken at about 60 different points of the field. Of those oscillograms 20 are reproduced in this communication (see Plate I—IV). The electrical arrangement was essentially the same as described in „Mededeeling 21". As the apparatus for periodic short circuiting described there did not work satisfactorily in consequence of perturbations caused by the rubbing contact, a key with platinum contacts is now used, which is moved up and down automatically, by means of a rotating notch.

The calibration was repeated frequently between the taking of the records. The arrangement proved to be satisfactorily constant. From the calibration curves a scale has been derived, which has been indicated on the oscillograms. The short straight segments of the records are caused by the short circuiting of the amplifier input; they determine the level of velocity $V = 7.45$ m/sec, that is, for all these records, the velocity at a great distance from the plate, known from the indication of Pitot tube and manometer (see fig. 1). Immediately before each of these straight segments, there are rapid deviations caused by the jumping back of the key before it keeps down finally. These deviations of course have nothing to do with airspeed fluctuations.

Time goes from left to right on the oscillograms; one period of the sine curve $= {}^1/_{50}$ sec.

Oscillograph characteristic and hot wire compensation were such, that airspeed fluctuations of frequencies up till about 1500 are reproduced correctly.

6. The oscillograms clearly illustrate the lability of the layer of discontinuity; it appears that fluctuations of the velocity arise in this layer and rapidly increase in downstream direction. This may be an indication of the dividing up of the layer into separate vortices.

If we consider the state of things immediately behind the leading edge ($x = 1.3$ mm and $x = 2.3$ mm), then we see that both above and under the narrow region of strong rotation the motion is nearly steady (see osc. N°. 2 and 3). Within the region mentioned there are irregular fluctuations, both slow waves with a period of f.i. ${}^1/_{10}$ sec., and more rapid ones of f.i. ${}^1/_{300}$ sec, superposed on each other (N°. 1, 4 and 5).

These fluctuations grow more marked when going downstream. Besides, at $x = 3.3$ mm and more distinctly at $x = 4.3$ mm we can see the first indication of much more rapid fluctuations, visible as sharp little peaks on all waves of the recorded line (record N°. 6). The amplitude of these fluctuations of high frequency increases rapidly. At $x = 5.3$ mm (N°. 7, 8, 9 and 10) they are sometimes already very great. It must be noted that

PLATE I.

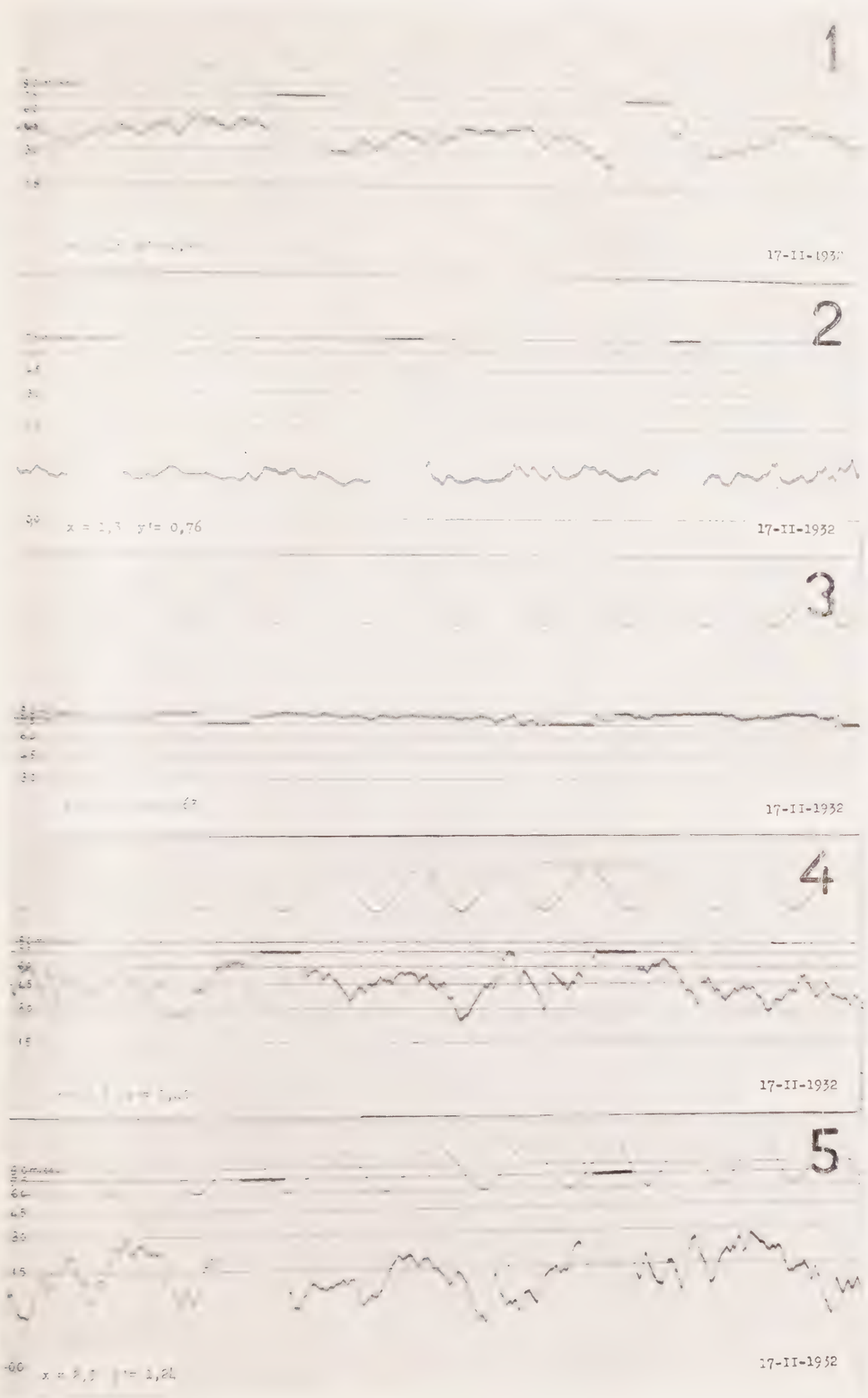
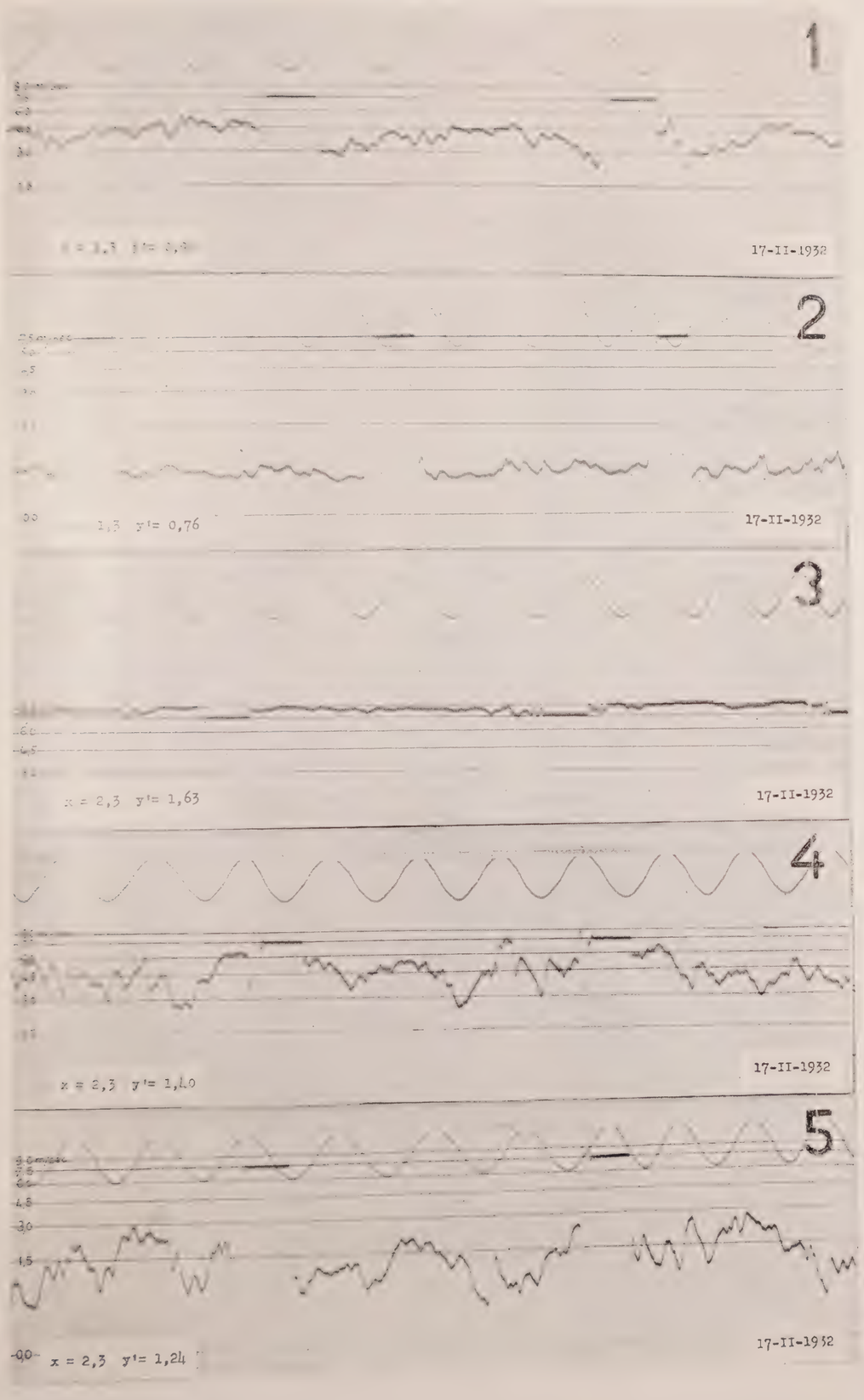


PLATE II

PLATE I.


1
17-II-1932
2
17-II-1932
3
17-II-1932
4
17-II-1932
5
17-II-1932

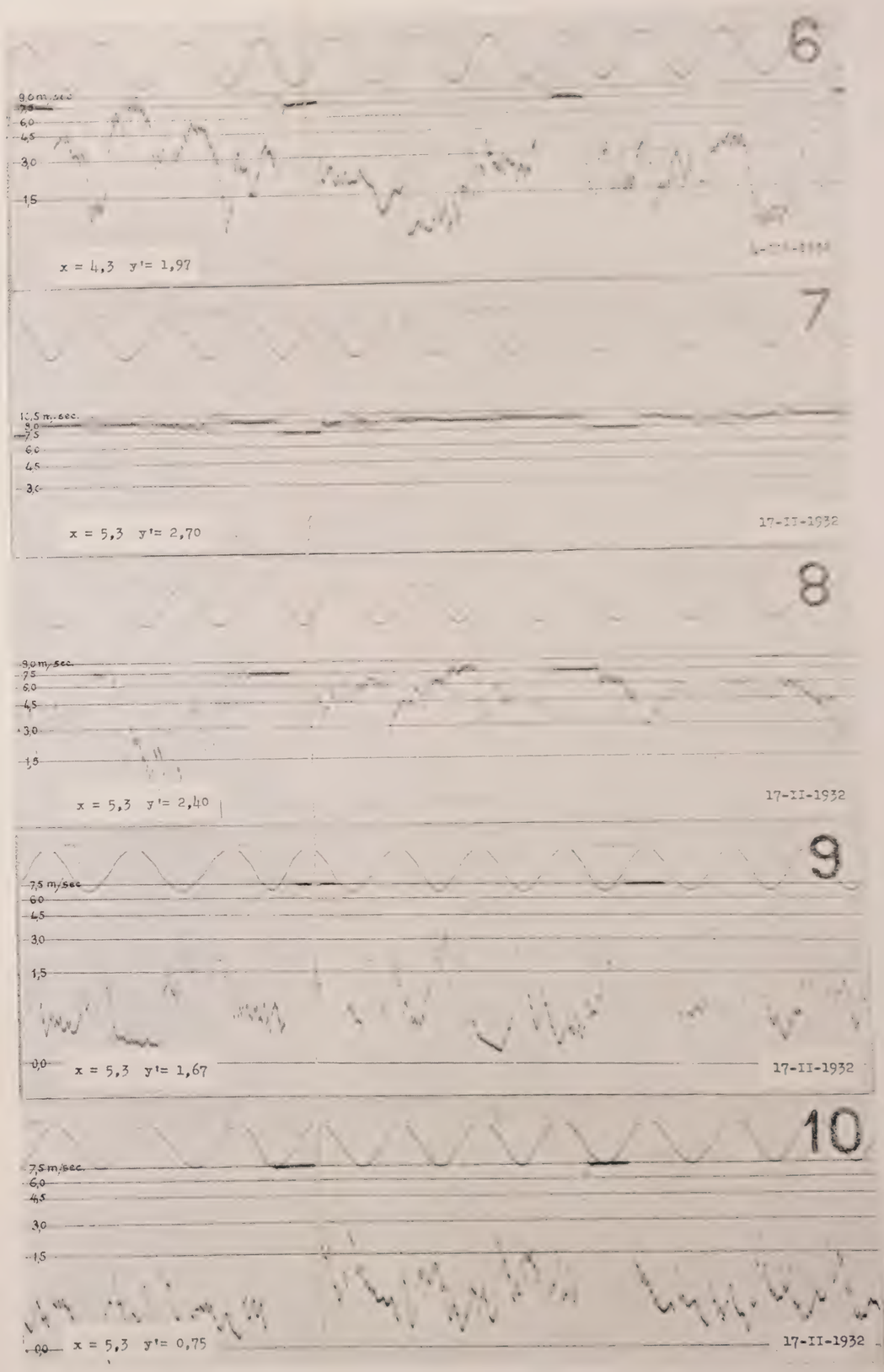

6
x = 4,3 y'= 1,97
7
x = 5,3 y'= 2,70
17-II-1932
8
x = 5,3 y'= 2,40
17-II-1932
9
x = 5,3 y'= 1,67
17-II-1932
10
x = 5,3 y'= 0,75
17-II-1932

PLATE III.

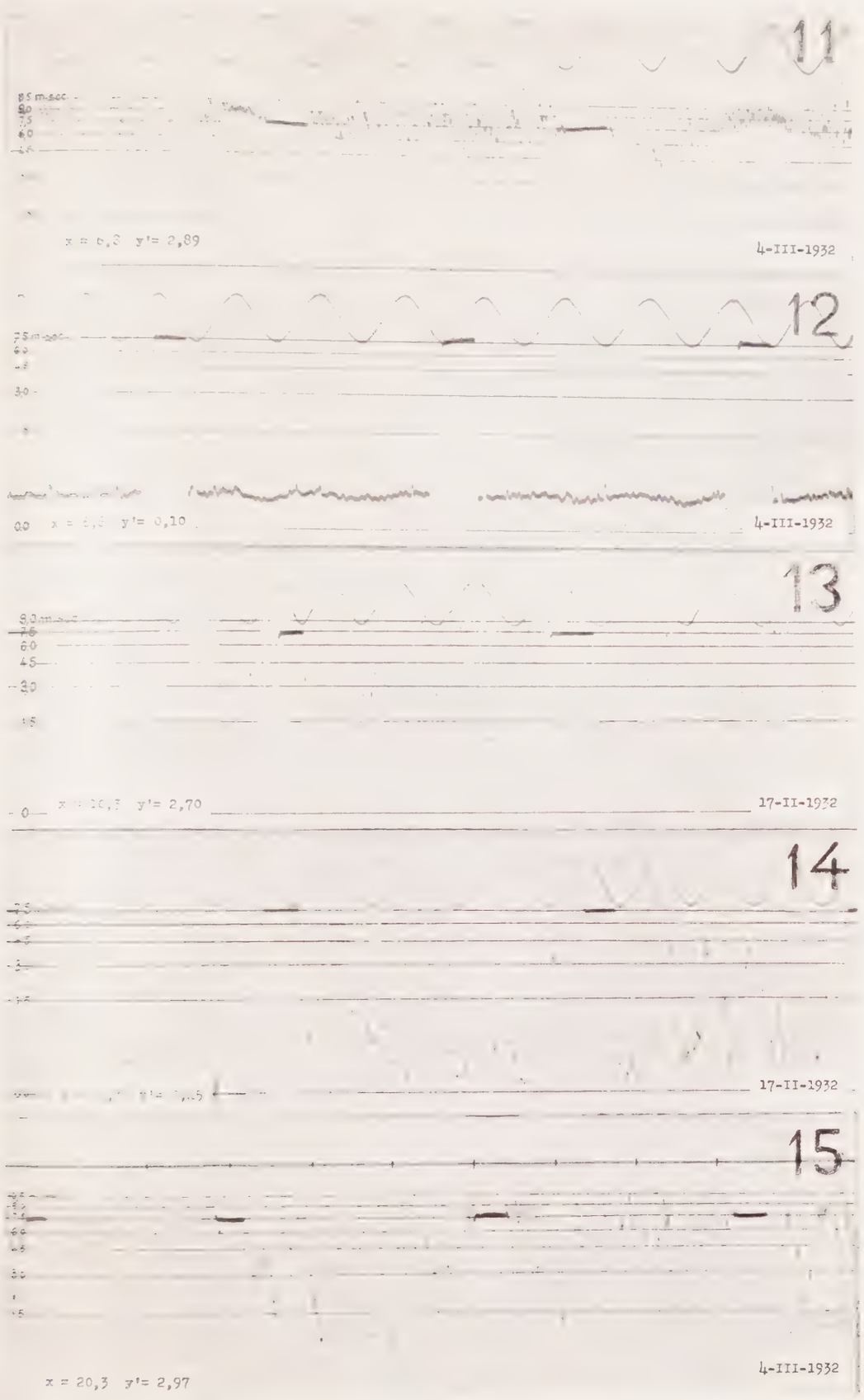
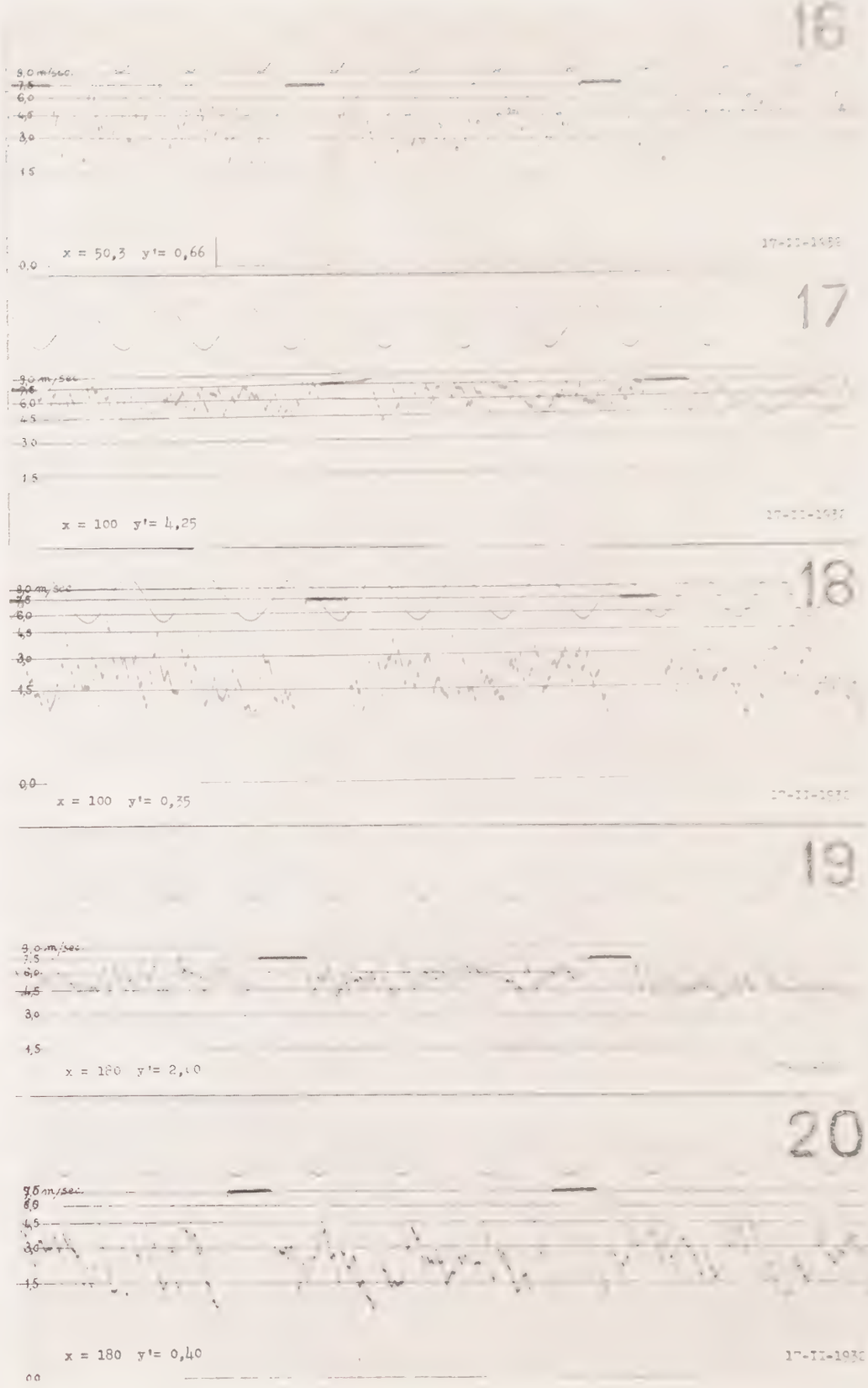



PLATE IV



these rapid fluctuations have much more penetrative power into the region of steady flow than the slow waves, which for $x = 5.3$ mm still are the most important within the region of strong rotation. The record which is taken at a point above that region (N°. 7, $y' = 2.70$ mm) practically does not show anything of these slow fluctuations, while the rapid ones can reach a value of more than 3 m/sec (see also osc. N°. 11 where this phenomenon still is more pronounced).

The reader will remark on the two last mentioned oscillograms that the rapid fluctuations undeniably show a certain regularity in their periods. This fact is confirmed by noting the sound produced by a loudspeaker connected to the amplifier. There is a noise of peculiar high pitch, which disappears when the hot wire is moved towards the leading edge. The pitch of this noise depends on the airspeed.

For $x = 5.3$ mm and further downstream, the region below the layer of discontinuity also has become turbulent. In contrast with what we remarked above, it appears that here the slow fluctuations now predominate; the rapid fluctuations are extinguished; it was noted that the high pitch of the noise from the loudspeaker disappears if the wire comes near to the wall. This phenomenon can be explained if it is assumed that the velocity of propagation of the disturbances is determined by the motion of the fluid particles themselves, which in the neighbourhood of the wall is much less than at greater values of y'.

Very near to the surface, all fluctuations are extinguished. The measurements here are influenced by the cooling of the wire by the wall, which causes a decrease of the sensitivity. It is thus difficult to get exact data. In taking the oscillogram N°. 12, which illustrate the state of things very near to the wall, the cooling effect of the latter has been compensated by increasing the heating current, so that we probably may assume that the normal calibration will not be much in error.

From $x = 10$ mm to $x = 20$ mm the turbulence has reached its maximum (see osc. N°. 13, 14, 15). The extreme amplitude of the perturbations measured here could hardly be expected in advance. Within intervals of $^1/_{3000}$ sec. the velocity can change from 1 m/sec to 9 m/sec. The great exchanges of energy connected with this "super-turbulence" wholly whipe out the discontinuity of the velocity, and from about $x = 50$ mm downward one has to do with the normal velocity curve of a turbulent boundary layer. The turbulent character there has lost much of its violence (osc. N°. 16). There is still a light decrease down to $x = 100$ mm (N°. 17 and 18), but after this point no further appreciable changes are remarked, as is shown by the oscillograms for $x = 180$ mm (N°. 19 and 20). It will be seen that not only the intensity of the fluctuations has decreased, but also their mean frequency; besides it appears both from the oscillograms and from the sound emitted by the loudspeaker, that the more or less periodic character of the rapid fluctuations (which was remarked for smaller values of x) has disappeared here.

7. It must not be lost out of sight that all these oscillograms give only an approximate reproduction of the velocity fluctuations at a given point, as certain distortions are inherent to the hot-wire and to the whole anemometer arrangement.

The principal causes of distortion are the lag of the complete arrangement [1]): the dimensions of the wire compared with the dimensions of the smallest homogeneous air particles; the unequal sensitivity of the hot-wire for the 3 velocity components of the airstream [2]); the increase of sensitivity for decreasing velocities.

The first three points are connected immediately with the problem of the fine structure of a three dimensional turbulent field, on which we hope to publish later some qualitative and quantitative data. The last point is the origin of the non linear character of the velocity scale, and, as was remarked already before, causes a too low indication of the mean velocity in a turbulent stream. The error is the less negligible, the greater is the amplitude of the velocity fluctuations. Exact measurements thus require a linear calibration curve. Investigations are carried out in this laboratory in order to improve the present methods of measurement.

Nevertheless it may be expected that, also without any correction, the oscillograms retain their value as an image of the character of the flow at various points of the field.

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[1]) Owing to the great convenience obtained by using sensitive oscillograph systems (SIEMENS & HALSKE, type V, suitable here uptill 1500 per.) and the presence still of other sources of distortions, the frequency limit has not been brought up to a higher value. For reliable quantitative investigations, this would be necessary however, though quite correct lag compensation would not be possible without more, as the lag of the hot wire is a function of the air velocity and thus compensation also has to vary with it. For details about the compensation of the lag of a hot wire the reader may be refered to these Proceedings, 33, p. 723, 1930. M. ZIEGLER, The application of the hot-wire anemometer for the investigation of the turbulence of an airstream.

[2]) The presence of an important component of the velocity fluctuations in the boundary layer, perpendicular to the x—y plane, has been ascertained by special experiments, to be described later.

Physics. — *Messmethoden zur Untersuchung der Wärmeabgabe von Lokalheizapparaten, besonders Radiatoren.* II. (Mitteilung aus dem Laboratorium der „Warmtestichting" Utrecht, Physikalisches Institut.) Von E. F. M. VAN DER HELD und L. L. MULDER. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of February 27, 1932).

Eichung des Apparates.

Die folgenden Messungen mussten ausgeführt werden:

1°. Eichung bei Zimmertemperatur.

2°. Bestimmung der Winkelabhängigkeit.

3°. „ „ Temperaturabhängigkeit.

Die Eichung bei Zimmertemperatur.

Um den Zusammenhang zwischen Torsionswinkel und Luftgeschwindigkeit zu bestimmen, war ein regelbarer Luftstrom nötig, der ausserdem in absoluter Grösse bekannt sein musste. Diese wurde im Strömungsfelde gefunden, das sich vor der Saugöffnung eines Ventilators formt, der aus einem grossen Raum ansäugt. Um dieses Feld für Berechnung zugänglich zu machen wurde die Saugöffnung in einer ebenen Wand angebracht. Man bekommt dann Zuströmung aus einem Halbraum (Abb. 9). Bei Entfernungen die gross sind gegen den Radius der Saugöffnung sind die Flächen mit gleicher Geschwindigkeit konfokale Rotationsellipsoïden, deren Hauptachsen mit der Achse der Öffnung zusammenfallen, und deren Brennpunkte in dem Rand der Öffnung liegen. Bei stationärer Strömung ist die Geschwindigkeit in jedem Punkte umgekehrt proportional mit dem Flächeninhalt des Ellipsoïds, das von diesem Punkte bestimmt wird. Die Dichteänderungen sind zu vernachlässigen.

Es ist also eine relative Eichung durchzuführen, indem man bei konstant belastetem Ventilator den Apparat in verschiedenen Entfernungen von der Öffnung aufstellt und den Torsionswinkel bestimmt.

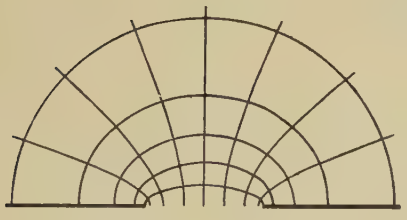

Abb. 9

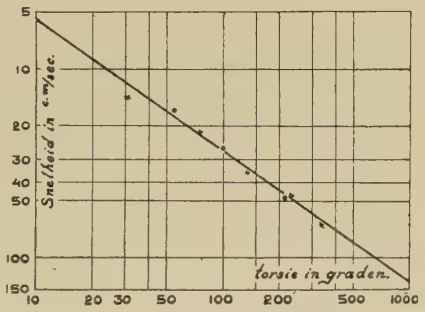

Abb. 10

Die Eichkurve war bei logarithmisch Auftragen von Geschwindigkeit und Torsionswinkel eine Gerade. (Abb. 10.) Nennt man den Torsionswinkel φ, die Kraft auf das System K, die Geschwindigkeit u, so gilt, weil φ proportional mit K ist:

$$K \backsim u^{5/4}.$$

Die gesammte vom Ventilator eingesogene Luftmenge konnte aus dem statischen Unterdruck berechnet werden, welcher sich in einer kurzen bekannten Entfernung vor der Saugöffnung einstellt. Diese Druckbeobachtung wurde an einer Reihe von Punkten durchgeführt, die gleichmässig auf dem axialen Schnitt eines Ellipsoïds verteilt lagen. Der Druck war auf dieser Ellipse nicht mehr gleichmässig weil zufolge der Nähe der Öffnung die Stromlinien stark gekrümmt sind und also die Masse der Luft eine Rolle spielt. Die Schwankung war aber klein genug um den Mittelwert der Beobachtungen für das ganze Ellipsoïd zu benutzen.

Wendet man auf dem Strömungsfeld ausserhalb des Messellipsoïds die Strömungsformel nach BERNOULLI für die inkompressibele Flüssigkeit an, so ist aus dem mittleren Unterdruck gegen den Druck des Raumes die mittlere Luftgeschwindigkeit auf dem Ellipsoïd zu berechnen und die eben genannte relative Kurve absolut fest zu legen.

Zur Bestimmung des statischen Druckes war vor der Öffnung ein axial gerichteter Metallschirm gelötet, der mit gleichmässig auf einer Ellipse verteilten Löchern versehen ist (siehe Abb. 11). In diese Löcher wurde die Mündung eines gut passenden Glasröhrchens gelegt so dass es an der anderen Seite noch nicht herausragte. Die Luft im Röhrchen nimmt den statischen Druck im Loch an, welcher mit einem Mikromanometer gemessen wurde. Kontrollversuche mit einer Scheibe nach SER ergaben gleiche Resultate.

Die Ergebnisse dieser Absolutmessung sind in Abb. 10 eingetragen. Es wurde bei drei Durchflussmengen gemessen, die man einstellen konnte durch verschiedene Blenden auf dem Druckstutze des Ventilators anzubringen. Die relative Kurve ist unter Beibehaltung seiner Neigung nach den drei absolut gemessenen Punkten verlegt, wobei mit der Ungenauigkeit der niedrigsten Durchflussmenge Rechnung gehalten wurde[1]).

Der Einfluss der Einfallrichtung.

Der Apparat wurde in einem einfachen, senkrecht gerichteten Windkanal unter verschiedenen Winkel α gegen die Strömungsrichtung aufgestellt. Bedeutet u die Luftgeschwindigkeit, so ist $u \cos \alpha$ die Geschwindigkeitskomponente senkrecht auf die Ebene des Sternchens. Weil die Luftgeschwindigkeit und die Kraft bei $\alpha = 0$ etwa linear zusammen hangen, war zu erwarten, dass die Kraft sich auch bei Änderungen von α proportional mit $u \cos \alpha$ ändern werde.

Abb. 12 gibt bei verschiedenen Einfallwinkeln die Geschwindigkeits-

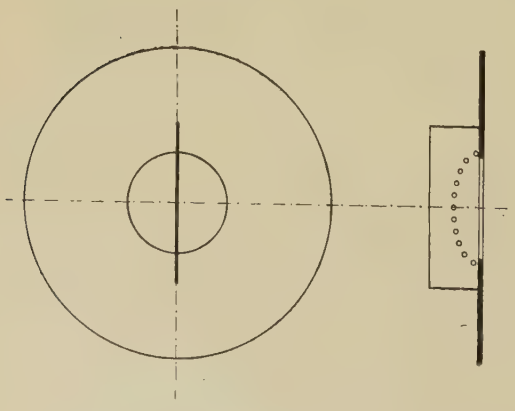

Abb. 11

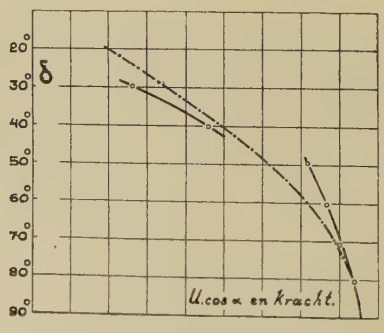

Abb. 12

[1]) Abb. 10 gilt für eine neuere Ausführung des Sternchens; die Neigung der Kurve hat sich daher geändert.

komponente in der Normalrichtung des Sternchens (punktierte Kurve) und die beobachtete Kraft (ausgezogene Kurve).

Weil bei Radiatoren die Luft fast überall senkrecht emporsteigt und die Abweichungen aus dieser Richtung maximal 30° betragen, kann man die senkrechte Geschwindigkeitskomponente messen indem man das Sternchen immer in den wagerechten Stand zurückdreht (Der Fehler beträgt maximal 5 % ; ausserdem treten die grössten Werte auf in den Stellen, wo die Übertemperatur der Luft sehr gering ist).

Die Temperaturabhängigkeit.

Um diese Grösse zu bestimmen, wurde oben im Windkanal ein elektrisches Heizgitter aufgestellt. Unter dem Heizgitter stand der Windmesser. In dieser Weise konnte man also beliebig kalte oder warme Luft durch den Windkanal saugen und bei gleichbleibender Luftmenge, aber verschiedener Temperatur (15° und 63° C.) den zugehörigen Torsionswinkel bestimmen. Wir fanden, dass:

$$\frac{k_{63}}{k_{15}} = 1.3$$

Dieser Effekt ist wie folgt zu erklären:

Nennt man μ den Reibungskoeffizient der Luft,
ϱ die Dichte der Luft,
$\gamma = \frac{\mu}{\varrho}$ den kinematischen Reibungskoeffizient,
u die Geschwindigkeit,
k die Kraft auf dem Sterchen,

und beobachtet man zwei Strömungszustände 1 und 2 bei den Temperaturen a und b, so kann man 1 und 2 vergleichen, indem man einen Zustand 3 zwischenschaltet, und dabei für 1 und 3 gleiche Temperatur und für 2 und 3 denselben Wert der REYNOLDschen Zahl annimmt. Nennt man letztere R, so ist:

$$R_3 = R_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Nun ist $R = \frac{\varrho l u}{\mu}$, worin l eine beliebige Abmessung des Sternchens, also eine Konstante bedeutet, sodass sich aus (I) folgert:

$$\frac{\varrho_3 u_3}{\mu_3} = \frac{\varrho_2 u_2}{\mu_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

In diesen beiden Fällen (3 und 2) sind nun die Kräfte nicht gleich, aber wohl die dimensionslosen Grössen:

$$\frac{k_3}{\varrho_3 l_3^2 u_3^2} = \frac{k_2}{\varrho_2 l_2^2 u_2^2}$$

oder, weil die Abmessungen gleich bleiben:

$$\frac{k_3}{\varrho_3 u_3^2} = \frac{k_2}{\varrho_2 u_2^2}$$

Es war oben experimentell festgestellt, dass

$$\frac{k_1}{u_1^{5/4}} = \frac{k_3}{u_3^{5/4}}$$

Man findet also für das gesuchte Kräfteverhältnis:

$$\frac{k_1}{k_2} = \frac{k_1}{k_3} \times \frac{k_3}{k_2} = \frac{u_1^{5/4}}{u_3^{5/4}} \times \frac{\varrho_3 u_3^2}{\varrho_2 u_2^2},$$

oder weil $u_1 \varrho_1 = u_2 \varrho_2$; $\varrho_1 = \varrho_3$ und $\mu_1 = \mu_3$ ist, und also aus (II) ausserdem folgt, dass $\frac{u_3}{\mu_3} = \frac{u_1}{\mu_2}$ ist;

$$\frac{k_1}{k_2} = \frac{u_1^{5/4}}{u_3^{5/4}} \times \frac{\varrho_2 \varrho_1 u_3^2}{\varrho_1^2 u_1^2} = \frac{\varrho_2}{\varrho_1} \cdot \frac{u_3^{3/4}}{u_1^{3/4}} = \frac{\varrho_2 \mu_1^{3/4}}{\varrho_1 \mu_2^{3/4}}$$

Nimmt man für a 63° und für b 15° C., so ist $\frac{\mu_1}{\mu_2} = 1.13$, sodass

$$\frac{k_1}{k_2} = \frac{336}{285} \times 1.13^{3/4} = 1.3$$

was sehr gut mit dem gefundenen Wert übereinstimmt.

Die Übertemperaturen, welche beim Radiator vorkommen, sind gewöhnlich nicht höher als 30° C. Für diesen Fall darf man in erster Näherung $\left(\frac{\mu_1}{\mu_2}\right)^{3/4} = 1$ nehmen, sodass man für die Geschwindigkeit nur eine Dichtekorrektur anzubringen braucht. Für die maximale Differenz von 30° ist der Fehler etwa 4 %, für die Gesamtwärmeabgabe viel geringer.

Die Temperaturmessung.

Bei dieser Messung wurde ein blank geschmirgeltes horizontal ausgespanntes Thermoelement aus Kupfer-Konstantan benutzt, von dem die Eichungskurve bekannt war. Zwischen dem Kupfer- und dem Konstantanteil wurde ein Stück Manganine gelötet, das in die Kombination mit Kupfer fast keine Thermokraft ergab, wohl aber die Wärme viel schlechter leitete als letzteres. In dieser Weise konnte auch in einem Gebiet mit starkem Gradient die Lufttemperatur genügend Stellenweise gemessen werden. Die zweite Lötstelle wurde unter dem Radiator aufgestellt. Eine Abschätzung des Strahlungseinflusses ergab, dass dieser zu vernachlässigen ist.

Messungen am Radiator.

Die Messungen von Geschwindigkeit und Temperatur wurden so aus-

geführt, dass immer auf parallele Geraden (z.B. parallel zur horizontalen Hauptachse des Radiators) in gleichen Distanzen von etwa 5 cm. Messpunkte lagen. Die gefundenen Ablesungen wurden graphisch verwertet in Kurven, denen man die Stellen entnahm, wo die senkrechte Geschwindigkeitskomponente 4, 8, 12 ..... 16 cm., u.s.w. bzw. die Übertemperatur 2, 4 u.s.w. ..... 30° C. betrug. Weiter wurden diese Stellen in zwei Karten angegeben, und durch Linien gleicher Geschwindigkeit, bzw. gleicher Übertemperatur verbunden. (Abb. 13 und 14).

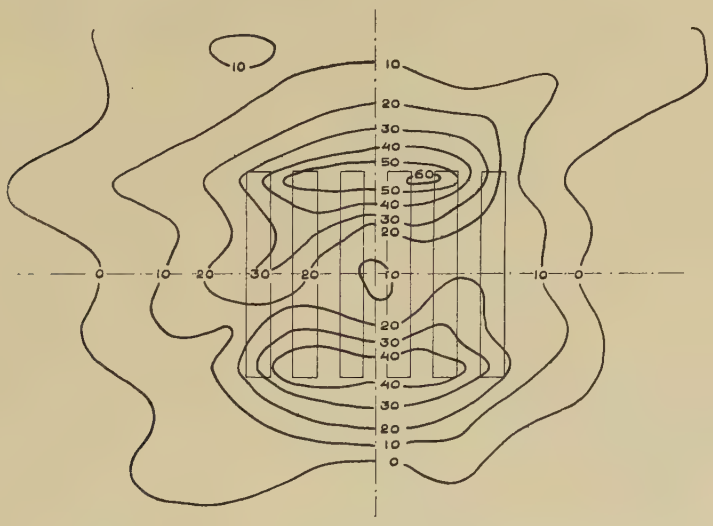

Abb. 13

Abb. 14

Die gesamte, durch die Messebene strömende Wärmemenge ist die Summe der Anteile, welche durch jedes Flächenelement hindurchtreten. Es hat keinen Zweck, die Grösse dieser Elemente kleiner zu wählen als die wirksame Fläche des Geschwindigkeitsmessers.

Es wurde ein Netz von 2×2 cm^2. benutzt. Die die Messebene durchströmende Wärmemenge beträgt:

$$Q = \sum_{k=1}^{k=n} v_k \times \theta_k \times S_{T_k} \times c_p \; {}^{k\,kal}/_{sek}$$

wenn v = die senkrechte Geschwindigkeitskomponente in cm/sek.

θ = die Übertemperatur der Luft in °C.

S_T = das spezifische Gewicht der Luft bei T°C.

c_p = die spezifische Wärme der Luft bei konstantem Druck.

n = die Zahl der Quadrate, worauf die Berechnung ausgedehnt ist.

Es ist, wenn H der Luftdruck in cm. Hg und P der Teildruck des Wasserdampfes bedeutet:

$$c_p = \tfrac{1}{776} \{(H-P)\,0.241 + P \times 0.46\} \; {}^{k\,kal}/_{gr}$$

Für T ist angenommen $20 + \theta$ (Lufttemperatur gleich 20 + Übertemperatur); ist die Zimmertemperatur nicht 20° C. aber t°C. so kann man den ganzen Ausdruck multiplizieren mit dem Faktor:

$$1 - \frac{t - 20}{320}$$

Der Nenner 320 ist die nur abgeschätzte absolute Temperatur der emporsteigenden Luft.

Für die Geschwindigkeitsmessung braucht man keine Korrektur mehr anzubringen, weil die Dichtekorrektur auch hierfür genügt.

Resultate der Konvektionsmessung.

Die Distanz des Radiators von der Zimmerwand betrug etwa ein Meter, um die Strömung möglichst störungsfrei zu erhalten. Die Feuchtigkeit der Luft wurde mittels eines Aspirations-hygrometers nach ASSMANN bestimmt.

Schon etwa 2½ Stunden nach der Inbetriebsetzung war die Wärmeabgabe genügend konstant geworden um die Messungen anzufangen, aber das Gleichgewicht des Zimmers stellte sich nicht innerhalb 4 Stunden ein.

Die Beobachtungen wurden in einer Ebene auf 21 cm. Höhe über die Achse des oberen Verteilrohres ausgeführt.

Die erhaltenen Diagramme sind nicht genau symmetrisch, was den nicht idealen Verhältnissen zuzuschreiben ist, welche im Anfang dieses Aufsatzes schon beschrieben wurden. Weiter stellte sich heraus, dass die Geschwindigkeitsmaxima sich beiderseits des Verteilrohres befinden. Die Strahlen, welche aus jedem Zwischenraum emporsteigen sind in der beobachteten

Ebene nicht mehr zu finden. Sie mischen sich bald nachdem sie den Radiatorkopf verlassen um zu einer wirbelnden Säule empor zu steigen.

Die durch Konvektion abgegebene Wärmemenge betrug:

$$713\ ^{k\,kal}/_{st}$$

bei einer Übertemperatur der Heizfläche von 57° C.

Die Strahlungsmessung (ausgeführt von Herrn C. A. CAMPAGNE).

Für diese Messung wurde eine Thermosäule benutzt. Es sollte damit der Wärmefluss durch irgend eine geschlossene Fläche, die den Radiator vollkommen umschliesst bestimmt werden indem man die Grösse der Normalkomponente an jeder Stelle misst. Wir wählten eine Kugel von 1 m. Radius, beschrieben um den Mittelpunkt des Radiators. Die Thermosäule sollte dann immer auf den Mittelpunkt gerichtet sein und jede Stelle der Kugel sollte man erreichen können. Dazu wurde das Objekt drehbar um seine vertikale Achse aufgestellt, während die Säule um eine horizontale Achse durch den Mittelpunkt des Radiators drehen konnte.

Die Thermosäule[1]).

Die benutzte Oberflächenthermosäule (Abb. 15) besteht aus 15 Thermoelementbändern, bestrichen mit mattschwarzem Lack (Schwärzungsfaktor etwa 90 % bei einer Wellenlänge $\lambda = 8$ bis 9 μ). Da von jedem Bändchen aus der Radiator völlig sichtbar sein sollte, ist das Gehäuse in entsprechender Form ausgeführt. Es wurde kontrolliert, ob die von einem parallelen Lichtbündel erregte E.M.K. sich gleichförmig mit dem Kosinus des Einfallswinkels zwischen Bündel und Säulenachse änderte. Dies war nötig,

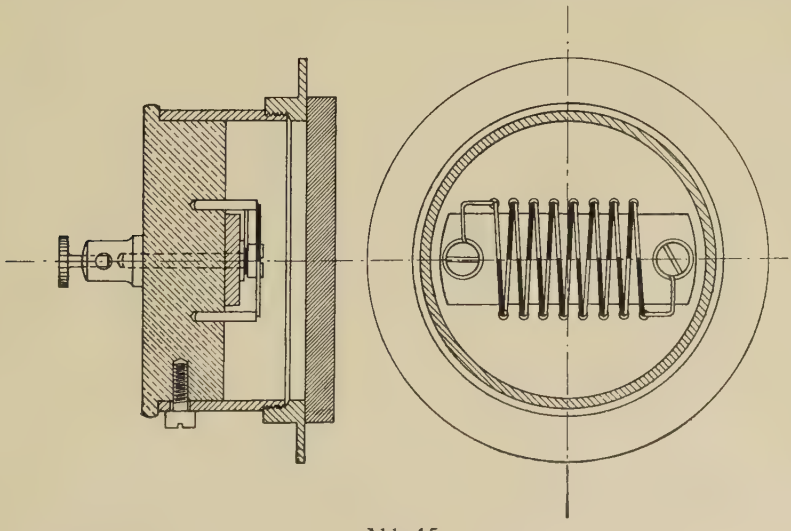

Abb 15.

[1]) Siehe auch für näheres über Thermosäulen. Proc. Phys. Soc. London **35** (1923) s. 257. Proc. Amsterdam **16** (1913) s. 568.

weil die Säule nur die Komponente der Strahlung senkrecht auf ihrer Fläche angeben sollte.

Diese Kontrolle stimmte genau. Die Säule war mit einer Steinsalzplatte verschlossen, deren gesammte Absorption und Reflexion im gleichen Wellenlängebereich wie während der Benutzung bestimmt wurde. Die unbedeckte Thermosäule wurde dazu an das eine Ende eines Papperohres gesetzt, mit dessen zweitem Ende die Steinsalzplatte lösbar verbunden wurde. Auch, wenn die Platte fort genommen war, war der Stand des angeschlossenen Galvanometers vollkommen ruhig. Es traten also im Rohre keine störende Luftströmungen auf. Bestrahlt man nun die Säule durch das Rohr mit einem Kubus von LESLIE, worin sich siedendes Wasser befindet, so wird das Verhältnis der Ausschläge des Galvanometers bei anwesender bzw. fortgenommener Steinsalzplatte die Durchlässigkeit der Platte ergeben. Dieser Wert war aber nicht konstant sondern bewegte sich zwischen 72 und 82 %. Dies ist nur zu erklären mit der Zunahme von variabelen Wasserschichten auf dem Steinsalze. Nach jeder Messung musste darum die Durchlässigkeit aufs neue bestimmt werden.

Benutzt man nun die Durchlässigkeit unmittelbar an der Säule, so hat man zu beachten, dass die von der Wasserschicht absorbierte Energie teils zurück gestrahlt und teils mit der durchgelassenen Strahlung auf die Thermobänder fällt. Infolge der kurzen Entfernung zwischen Steinsalz und Thermobändern im Verhaltnis zu der Fläche des Steinsalzes kann man annehmen, dass die Hälfte der absorbierten Energie sich zu der durchgelassenen Strahlung addiert. Hat man z.B. eine Durchlässigkeit von 75 % gefunden, so wird von dem Rest (25 %) etwa 7 % Reflexion sein und 18 % Absorption, wovon 9 % auch auf die Säule fällt und man misst mit dem Galvanometer also 84 % der auf das Steinsalz gefallenen Energie.

Der Kubus von LESLIE wurde auch zur Absoluteichung der Säule benutzt. Das Gefäss war mit einer Mischung von Russ und Wasserglas [1]) bestrichen, deren Schwärzung bekannt war (96 % des absolut schwarzen Körpers) und einen verschwindend kleinen Wärmewiderstand bildet. In einer doppelten Wand zwischen Kubus und Säule befand sich eine Öffnung, die so klein war, dass die auf die Säule fallende Strahlung als senkrecht einfallend angesehen werden konnte.

Zur Bestimmung des Nullpunktes des Galvanometers wurde ein doppelter Schirm von Weissblech benutzt, der beweglich zwischen beiden Schichten des grossen Schirmes angeordnet war und die Öffnung schliessen konnte.

In dieser Weise wurde der Eichwert festgestellt zu

$$1\,\mu V \sim 7.40 \times 10^{-6}\ watt/cm^2$$

bezogen auf die Energie, welche wirklich auf die Thermobänder fällt. Für

[1]) Nach E. SCHMIDT: Wärmestrahlung technischer Oberflächen bei gewöhnlicher Temperatur; und auch Ztschr. f. Physik **14**, S. 30 (1923).

die Messungen am Radiator soll noch die obengenannte scheinbare Durchlässigkeit in Rechnung gebracht werden.

Zur Kontrolle wurde die Thermosäule im sichtbaren Wellenlängengebiet verglichen mit einer Säule, die nach dem Verfahren von VAN DIJCK absolut geeicht worden war [1]). Der mattschwarze Lack auf den Thermobändern ist sowohl für sichtbare Wellenlängen als für das weitere ultrarote Gebiet etwa 90 % schwarz (± 5 %).

Die Vergleichung ergab:

$$1\,\mu V \sim 7.15 \times 10^{-6}\ watt/cm^2$$

also in guter Übereinstimmung mit dem obengenannten Eichwert, welcher bei unseren Messungen ausschliesslich benutzt wurde.

Ergebnisse der Strahlungsmessungen.

Für die Bestimmung des Nullpunktes der Säule wurde der Radiator mit einem Schirm aus Sperrholz abgedeckt, das an der zur Säule gekehrten Seite mit einer auf 2 cm. Abstand gestellten Aluminiumplatte versehen war.

Am höchsten Punkte der Kugel war die Messung nicht auszuführen, weil der Konvektionsstrom die Säule umspühlte und die Beobachtung unsicher machte.

Die Abschirmung durch den Tisch, auf den der Radiator gestellt war machte die Messungen an den niedrigsten Punkten der Kugel unmöglich. Es wurden diese Werte Schätzungsweise in Tafel I eingetragen. Ein Beispiel für die Strahlungsverteilung über einen horizontalen Parallelkreis der Kugel ist in Abb. 16 gegeben, wobei die radiale Komponente der

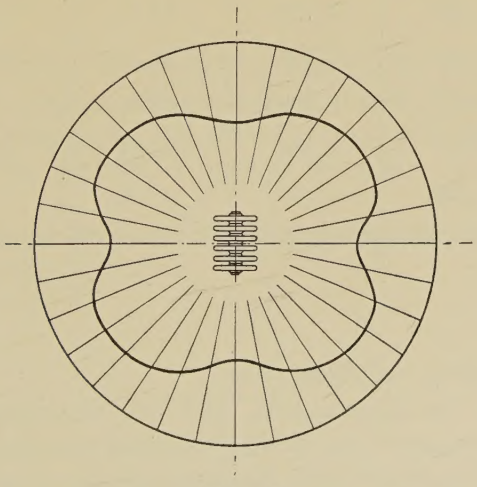

Abb. 16.

Strahlungsdichte der Kugelfläche auf dem zugehörigen Radius angegeben wurde.

[1]) Ztschr. f. Phys. Chem. Bd. **127** N⁰. 3/4, S. 249 (1927).

Die Minima liegen offenbar in den Richtungen, in denen man zwischen die Glieder oder Säulen hindurch sehen kann.

In Tafel I sind die Ergebnisse für verschiedene Höhen zusammen gestellt. Für die gesammte Wärmeabgabe durch Strahlung findet man:

$$293\ k\ kal/st$$

bei 57° C. mittlere Übertemperatur der Heizfläche.

TAFEL I.

Kugelring	Mittlere Winkel über der Hor. Ebene	Fläche des Ringes	mittlere Energie in Watt/M²	Gesamte Strahlung durch einen Ring in Watt.	
Polscheibe.	90°	0.053	(21.3)	1.1	geschätzt
I	75°	0.420	24.3	10.2	
II	60°	0.811	27.3	22.1	
III	45°	1.148	28.3	32.7	
IV	30°	1.1404	30.6	43.0	
V	15°	1.568	31.1	48.8	
VI	0°	1.622	30.0	48.7	
VII	—15°	1.568	29.7	46.5	
VIII	—30°	1.404	27.3	38.4	
IX	—45°	1.148	23.8	27.3	
X	—60°	0.811	(19.6)	22.3	geschätzt
	—75°	0.420	(13.9)		
	—90°	0.053	(10.5)		
				341.1 Watt = 293 k kal/st	

Zusammenstellung der Ergebnisse.

Die Resultate der Konvektions- und der Strahlungsmessung sind in Tafel II dem Ergebnis der Abkühlungsversuche gegenübergestellt. Es wurden auch die wesentlichsten Abmessungen u.s.w. beigefügt.

Die Summe der beiden Teilmessungen ist nicht gleich dem Resultate der Abkühlungsversuche. Dies ist hauptsächlich der Konvektionsmessung zuzuschreiben, weil diese am verwickeltsten ist und die Absoluteichung des Geschwindigkeitsmessers im Gebiet von 6 bis 60 cm/sek nicht genau möglich war. Eine ausführlicheres Verfahren ist in Ausarbeitung.

Die Ergebnisse der Strahlungsmessung fanden wir, in Übereinstimmung mit dem mittels der Formeln von THOMAS [1]) gefundenen Wert: 306.

TAFEL II.

Abmessungen: Höhe, ohne Füsse	85 cm.
Breite	28 „
Tiefe.	22 „
Dicke eines Gliedes	2.6 „
Entfernung der Glieder Mitte.	3.0 „
Gliederzahl	6 „
Säulenzahl	6 „
Eisen Gewicht des Radiators	67.9 KG.
Gewicht des Wasserinhalts.	9.0 „
Heizfläche	2.52 M^2.
Übertemperatur der Heizfläche	57° C.
Warmeabgabe durch Konvektion	713 k kal/st
„ „ Strahlung.	293 „ „
Konvektion und Strahlung zusammen	1006 k kal/st
Nach den Abkühlproben	1080 „ „

Wurde das beschriebene Messverfahren auch für Radiatoren entwickelt, so wird man sowohl die Konvektionsmessung, als die Strahlungsmessung auch auf andere Wärmequellen für Raumheizung anwenden können und sie mögen also zu deren schweren Studium beitragen.

[1]) THOMAS, Die Wärmeabgabe des Radiators, Beiheft Gesundheits Ing. Reihe I Heft 23.